

**Project title:** Conversion of oxyfluoride based coated conductors

Covering period: September 1<sup>st</sup>, 2003 through August 31<sup>st</sup>, 2006

Date of Report: November 29<sup>th</sup>, 2006

Recipient: Massachusetts Institute of Technology,  
77 Massachusetts Ave.  
Cambridge, MA 02139

Award number: DE-FC07-03ID14507

Subcontractors: N/A

Other partners: N/A

Contact(s): Michael J. Cima, 1-617-253-6877, mjcima@mit.edu

Project team: Masaki Suenaga, Brookhaven National Laboratory

**Objective:**

Direct measurements of HF pressure in equilibrium with the film during the BaF<sub>2</sub> process are sorely needed. It is the HF partial pressure that governs the rate at which the film composition is changing and is, therefore, an important factor in controlling the composition/time trajectory of the film. Establishing the composition/time trajectory of both MOD-derived and e-beam derived films for a given set of conditions is another goal for the project. These studies will provide a fundamental understanding of the *ex situ* process for producing coated conductors.

**Background:**

The BaF<sub>2</sub> process is commonly applied to fabricate high performance coated conductor cost-effectively. Oxyfluoride precursor is reacted with moisture to release HF gas with conversion of the film to YBCO. It has recently been shown that the HF gas removal from the YBCO growth interface limits the growth rate and has great influence on nucleation and growth morphology. We are focusing on physical and chemical reactions, including HF gas release, which occur prior to YBCO formation. P(HF) is measured using our unique method, the F/Ba trajectory is used to study chemical reactions, and film thickness is analyzed to study both physical and chemical reactions. Film thickness change is discussed from the viewpoints of sintering, release of HF gas, and other chemical reactions.

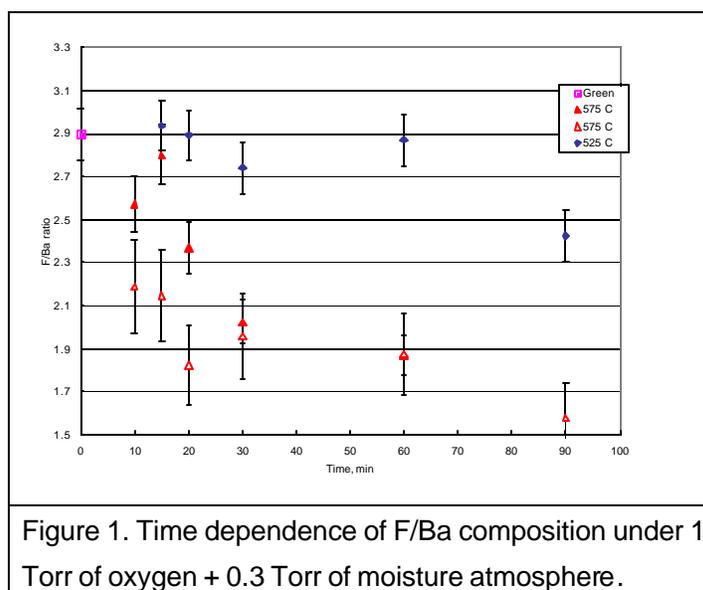
**Status:**

*FY2004*

XRD and fluorine to barium ratio measurement were done on MOD derived precursor films quenched at various temperature to investigate the reaction occurs prior to the nucleation of YBCO. A peak shift was observed at lower temperature due to the dissolution of  $YF_3$  into  $BaF_2$ . The shifted  $BaF_2$  peaks move back to the position of pure  $BaF_2$  with increasing temperature. No detectable YBCO peaks were observed below  $700^\circ C$ , even though the fluorine to barium ratio was below 2, which means  $BaF_2$  had begun to decompose to form BaO.

We constructed a Knudsen cell and measured the composition/time trajectory of MOD derived films. Several cells with different hole sizes were prepared so that the appropriate HF effusion rate could be established for each experimental condition.

Composition/time trajectories of MOD derived films were measured at different temperatures under 1 Torr of oxygen + 0.3 Torr of water pressure within Knudsen cells. The results obtained are shown in Figure 1. As shown in the figure, the trajectories have a bend point at about  $F/Ba=2$ , which is the boundary between the region of the decomposition of yttrium fluoride and that of barium fluoride. The fluorine loss versus time can be obtained from the composition/time trajectory shown in Figure 1. The resulting effusion rate can be used to calculate the partial pressure of HF using the Langmuir equation.



The calculated HF partial pressures shown in Table 1 vary with temperature

and extent of reaction from 0.03 to 0.2 Pa. The pressures when  $YF_3$  is still present are 0.028 to 0.17 at temperatures between 525 °C and 575 °C, respectively. Further reaction gives much lower pressures of 0.02 to 0.06 Pa at temperatures of 575 °C and 625 °C, respectively. All cases above have a fixed  $P(H_2O)$  of 0.3 Torr. Table 2 shows the calculated  $P(HF)$  obtained from the literature for two model reactions;

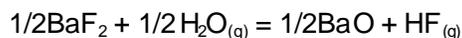
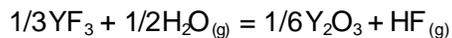


Table 3 shows the calculated partial pressure of HF expected for slightly more complex reactions;

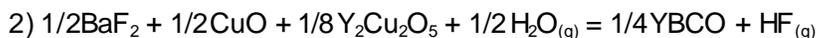
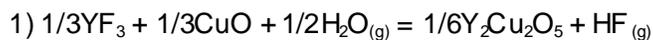


Table 1. Measured partial pressure of HF and calculated ? G of reaction				
Temp. °C	First step		Second step	
	$P_{HF}, \times 10^{-2}$ Pa	? G, kJ/mol-F	$P_{HF}, \times 10^{-2}$ Pa	? G, kJ/mol-F
525	2.8±0.3	74.1±0.8		
575	19±5	65.5±1.8	2.0±0.2	81.3±1.1
625			6.1±0.6	77.7±1.5

Table 2. Calculated partial pressure of HF and ? G of simple reactions obtained from literature.				
Temp. °C	YF <sub>3</sub> reaction		BaF <sub>2</sub> reaction	
	$P_{HF}, \times 10^{-1}$ Pa	? G, kJ/mol-F	$P_{HF}, \times 10^{-5}$ Pa	? G, kJ/mol-F
525	9.2	51.0		
575	23	47.7	1.93	122.0
625			25.7	118.8

Table 3. Calculated partial pressure of HF and ?G of the expected reactions obtained from literature				
Temp. °C	Reaction (1)		Reaction (2)	
	$P_{HF}, \times 10^{-1}$ Pa	? G, kJ/mol-F	$P_{HF}, \times 10^{-2}$ Pa	? G, kJ/mol-F
525	8.54-9.78	50.6-51.5		
575	21.9-24.5	47.3-48.1	0.245-36.1	60.8-96.0
625			0.79-95.7	57.1-92.9

As shown in the tables, experimentally measured P(HF) values of MOD derived films during the reaction of BaF<sub>2</sub> are within the range of literature values for formation of YBCO. On the other hand, P(HF) values measured during the reaction of YF<sub>3</sub> are not within the range of literature values of the predicted reactions to form intermediate compounds.

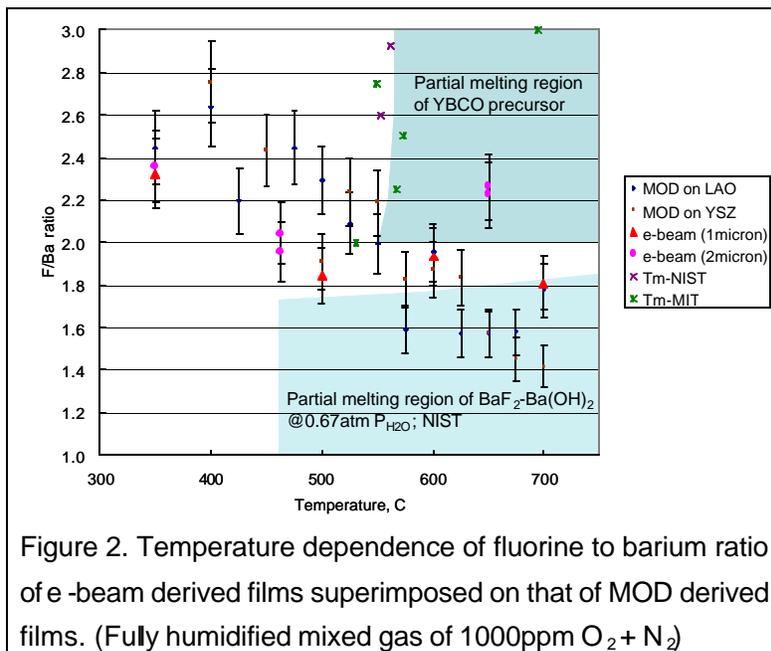
The equilibrium partial pressure of HF gas released by the decomposition of BaF<sub>2</sub> / YF<sub>3</sub> was also analyzed on MOD-derived BaF<sub>2</sub> films and MOD-derived YF<sub>3</sub> films. The data obtained from barium fluoride films is in good agreement with literature values, however the equilibrium P(HF) over yttrium fluoride films is quite different. P(HF) due to the decomposition of BaF<sub>2</sub> is quite low; therefore, the measurements were done at high temperature. However, barium loss was observed at higher temperatures (>785°C). The discrepancies in the region of the reaction of yttrium fluoride are thought to be caused by the presence of yttrium hydroxide or yttrium oxyfluoride. The presence of these compounds at high temperatures has recently been reported and may be the origin of a transient melt phase which supports highly oriented growth of YBCO from a substrate .

It was proven that YBCO formation from MOD derived oxyfluoride precursor proceeds in a few steps. The probable reaction steps are:

- 1) BaF<sub>2</sub>·YF<sub>3</sub> solution + CuO + H<sub>2</sub>O<sub>(g)</sub> = BaF<sub>2</sub> + Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub> + HF<sub>(g)</sub>
- 2) BaF<sub>2</sub> + H<sub>2</sub>O<sub>(g)</sub> = BaO + HF<sub>(g)</sub>
- 3) 2BaF<sub>2</sub> + 2CuO + 0.5Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub> + 2H<sub>2</sub>O<sub>(g)</sub> = YBCO + 4HF<sub>(g)</sub>

Analysis of e-beam derived films revealed that the fluorine removal rate and YBCO growth rate measured by conductivity are in good agreement with each other under same experimental conditions. This supports the theory that the removal of fluorine from a film limits YBCO growth.

Figure 2 is fluorine to barium ratio of e-beam derived films overlapped with that of MOD-derived films. The F/Ba ratio of e-beam derived film as deposited is around 2, which means no yttrium is present as oxyfluoride. XRD profiles do not show peaks shift like MOD films. The F/Ba ratio of e-beam derived film is not as sensitive to temperature as MOD derived films; however, e-beam green films have much lower F/Ba ratios. F/Ba in e-beam film does not drop significantly below 2, but the F/Ba ratio of MOD derived films drops down to 1.5 prior to YBCO formation. The F/Ba trajectory of both e-beam and MOD derived films slightly drop into partial melting region; however, the slopes of these trajectories are different. This indicates that e-beam derived films have a different amount of melt, composition of melt, starting temperature of YBCO formation etc. than MOD derived films.



The P(HF) measurement on e-beam derived films was performed. However, the effusion of HF gas from Knudsen cell into the atmosphere was not the rate-limiting step during the experiment, so the results did not indicate true P(HF). This could be the result of the high density of the precursor film.

#### FY2005

The FY2005 work focused on the detection of a low temperature melt by several circumstantial techniques, such as shrinkage measurements and F/Ba ratio trajectory. Measurements of film shrinkage were performed at low annealing temperatures and varying P(H<sub>2</sub>O). A discontinuity of about 7.5% in shrinkage vs. temperature was noted for MOD-derived films (Figure 3b). The discontinuity was dependent on P(H<sub>2</sub>O), occurring at 620°C under 22 Torr moisture and at 725°C under nominally dry gas (as-received) (Figure 3a). Little change in the F/Ba ratio trajectory was observed at these temperatures. This implies a discontinuity in sintering rate with increasing temperature. This could indicate the formation of a P(H<sub>2</sub>O) dependent melt. This suggests Ba(OH)<sub>2</sub> or BaF<sub>2</sub>-Ba(OH)<sub>2</sub> mixtures could be responsible for the low temperature melt. The reaction of BaF<sub>2</sub> and moisture to form Ba(OH)<sub>2</sub> is more likely to happen than that to form BaO because of its less positive  $\Delta G$ .

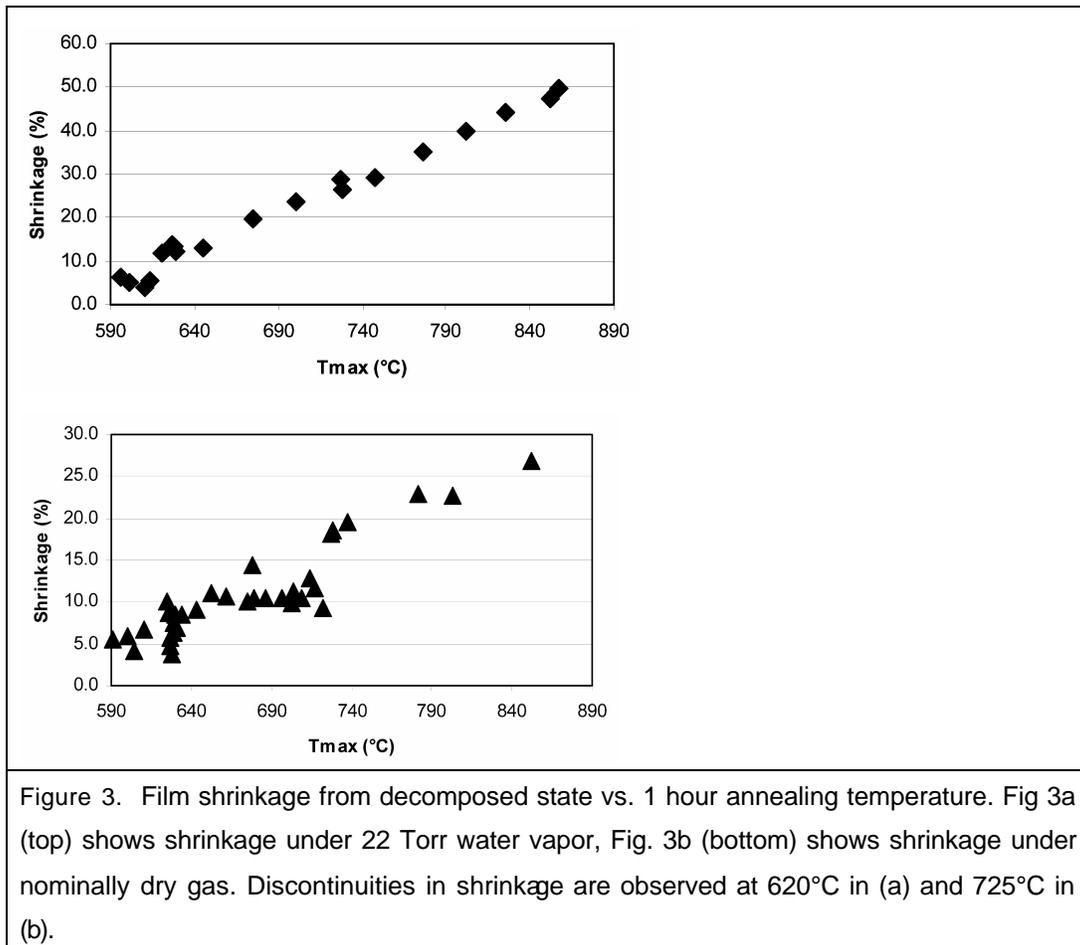


Figure 3. Film shrinkage from decomposed state vs. 1 hour annealing temperature. Fig 3a (top) shows shrinkage under 22 Torr water vapor, Fig. 3b (bottom) shows shrinkage under nominally dry gas. Discontinuities in shrinkage are observed at 620°C in (a) and 725°C in (b).

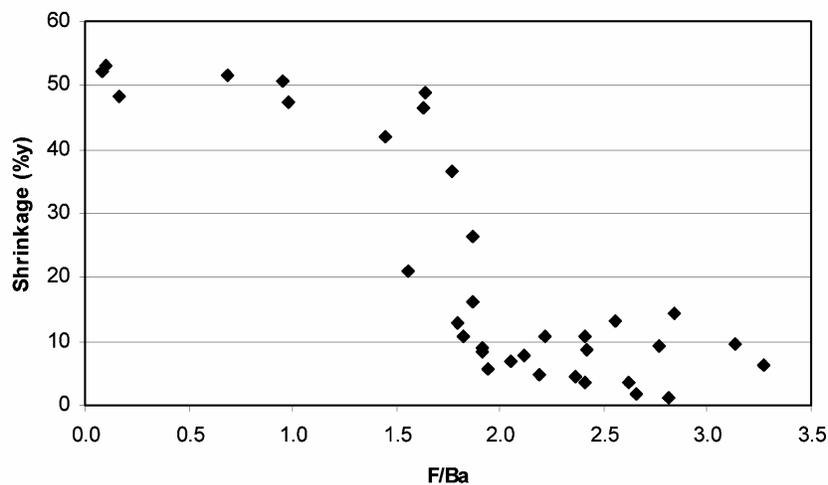


Figure 4. Film shrinkage from decomposed state vs F/Ba ratio in quenched films. A sharp increase in sintering rate is found across a compositional boundary of about F/Ba = 1.8.

Almost no shrinkage occurs during the decomposition of  $YF_3$  ( $F/Ba > 2$ ) and during the removal of around 80% of the  $BaF_2$  ( $F/Ba < 1.6$ ). This brackets a very small compositional region in which substantial shrinkage does occur. Figure 4 compares shrinkage to  $F/Ba$  across a wide range of processing conditions. A sharp increase in shrinkage is observed in the narrow  $F/Ba$  range 1.5-1.8. This accelerated sintering in a narrow compositional range suggests that crossing a compositional phase boundary lowered the sintering activation energy. This is further evidence of melt formation.

#### *FY2006*

The focus of work in FY2006 was relating the  $F/Ba$  trajectory to  $J_c$  in MOD-derived films. Data was collected for thick and thin films annealed at 760°C under three different partial pressures of water (~0.3, ~4, and 22 Torr). Figure 5 illustrates the results of these tests. The data indicates the removal of fluorine at relatively low temperatures is important, as suggested by earlier trials. XRD has indicated that YBCO nucleation begins around 700°C. The high  $J_c$  films have left (or soon leave) the fluorine-rich melt region when YBCO nucleation begins, while the low  $J_c$  films persist in the melt phase region to higher temperatures. The different nucleation environment may lead to very different nuclei density and / or orientation, causing the discrepancy in  $J_c$ .

High fluorine removal at low temperatures was obtained by using slow ramp rate (5°C/min) and high water vapor pressure (22 Torr). The difference between thick and thin films in  $F/Ba$  ratio under these conditions is small when compared to the effect of ramp rate and water vapor pressure. It was found that these new trajectories are not reliably high performance paths, suggesting an optimum  $F/Ba$  trajectory exists. Figure 1 illustrates the  $F/Ba$  trajectory vs. performance space. It was found that this trajectory produced high performance 800 nm films (average  $J_c = 1.2 \text{ MA/cm}^2$ ), regardless of whether high ramp rate and high  $P(H_2O)$  or low ramp rate and low  $P(H_2O)$  processing conditions were used. This means that trajectory, rather than ramp rate or  $P(H_2O)$ , controls film performance.

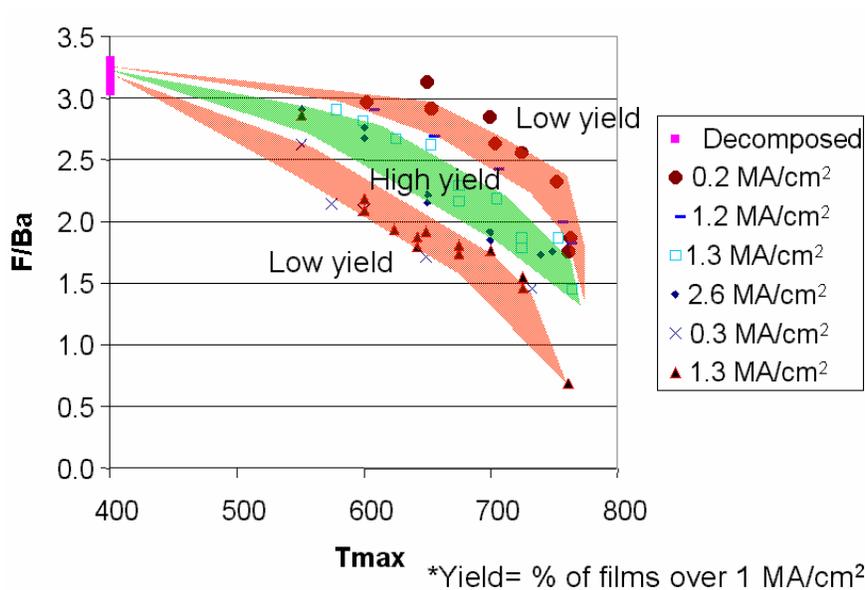


Figure 5. F/Ba ratio vs. temperature for several heat treatments and the  $J_c$  of those heat treatments.

XRD and microstructure studies help explain the reason for an optimal F/Ba trajectory. XRD was performed on a number samples on  $\text{CeO}_2$ -capped YSZ. The temperature at which the first (003) YBCO peak is detected in XRD varies from the annealing temperature ( $760^\circ\text{C}$ ) to less than  $700^\circ\text{C}$  depending on the trajectory. These results when compared to the trajectories (Figure 5) show that the onset of YBCO formation is related closely to a single F/Ba ratio, again indicating a compositional threshold must be crossed before YBCO can nucleate. The XRD data is not very precise, so the composition can only be described as between 1.5 and 2. This is exactly the range of composition where accelerated sintering occurs (Figure 4), implying YBCO forms in equilibrium with a melt phase.

The large variation in YBCO nucleation temperature resulted in large variation in the morphology of the YBCO grains. Figure 6 indicates performance and surface morphology for representative samples for thick films processed under all conditions. The samples that followed the optimal trajectory had little  $a$ -axis and few second phases visible on the surface. Samples that followed a high fluorine removal path had YBCO nucleate between  $650$  and  $700^\circ\text{C}$ .  $a$ -axis grains dominated these films, probably because of the large thermodynamic driving force for nucleation (large undercooling). Films with very low-fluorine removal trajectories had poor performance, but these microstructures did not show any  $a$ -axis grains.  $a$ -axis grains were not expected, as

these films are undercooled even less than films in the optimal trajectory. Figure 6 shows large second phases were present in these films. The long period of time at high temperatures in a melt region may cause second phases to ripen. These larger grains may not be consumed during YBCO growth, resulting in a film with significant compositional inhomogeneity.

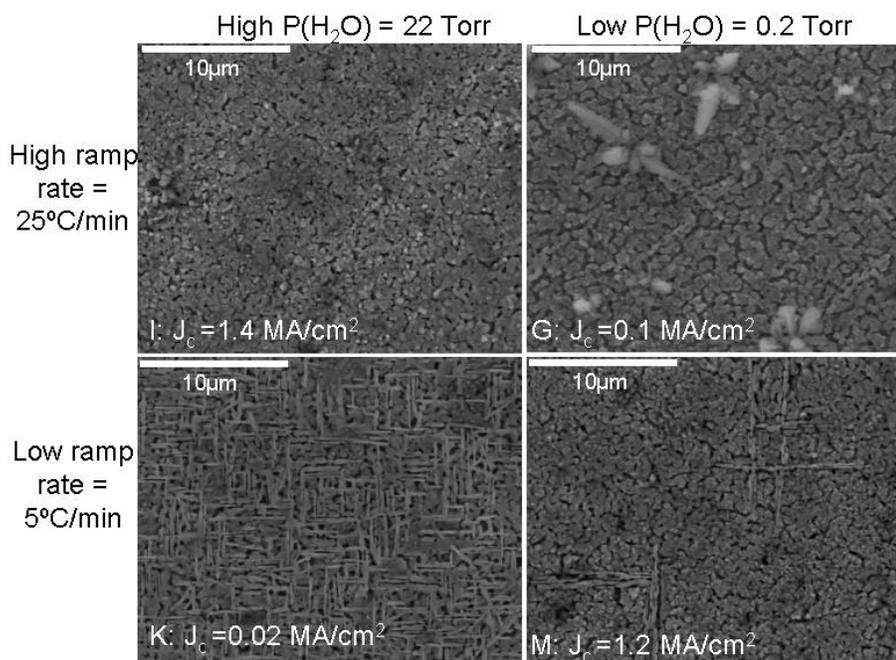


Figure 6. ~800nm film morphology under test  $P(H_2O)$  and ramp rate. Trajectories are the letters labeled on the figures. Nucleating YBCO below  $700^\circ C$  leads to significant  $a$ -axis growth.

A quantitative technique for measuring  $BaCeO_3$  formation was established in FY2006. A technique for solution deposition of  $CeO_2$  on YSZ was developed to aid in the rapid production of  $CeO_2$  cap layers; details can be found in the published work. Previous work had focused on detecting Ba depletion in overall film stoichiometry following a selective etch for YBCO over  $BaCeO_3$ . This established that the amount of Ba reacted during processing is easily detected by ICP. It was found that the selective etch for YBCO (pH 3.25  $HNO_3$ ) was not selective enough for quantitative work. It was found that  $BaCeO_3$  dissolves readily in 10%  $HNO_3$ , while  $CeO_2$  dissolves much more slowly. ICP was performed to detect Ce ions in solution. A  $CeO_2$  film on YSZ was soaked for 15hrs in 10wt%  $HNO_3$  and the solution tested for Ce ions to check for

dissolution of ceria. The Ce ion concentration was 51 ppb, which corresponds to 5% of the film. Films soaked for 10 minutes had Ce ion concentrations below the accurate detection limit of the system. XRD was used to establish that BaCeO<sub>3</sub> and YBCO both completely dissolve after 10 minutes in 10% HNO<sub>3</sub>.

Quantitative measurements of BaCeO<sub>3</sub> formation were performed after the selectivity of the 10% HNO<sub>3</sub> for BaCeO<sub>3</sub> over CeO<sub>2</sub> was established. The results are shown in Figure 7. It was found that little BaCeO<sub>3</sub> forms during ramping, and BaCeO<sub>3</sub> growth follows a parabolic rate law while annealing at temperature. These results match those reported by NIST at the Spring 2006 MRS meeting. Our technique also reveals that almost the entire CeO<sub>2</sub> film reacts with Ba during a 2hr anneal at 760°C. CeO<sub>2</sub> was formed by a solution deposition method; the amount of Ce in a film was determined by dissolving a as-spun films. 90% of this amount of Ce was detected in solution after reacting at 760°C for 2 hours, indicating that almost the entire CeO<sub>2</sub> film had reacted to form BaCeO<sub>3</sub>.

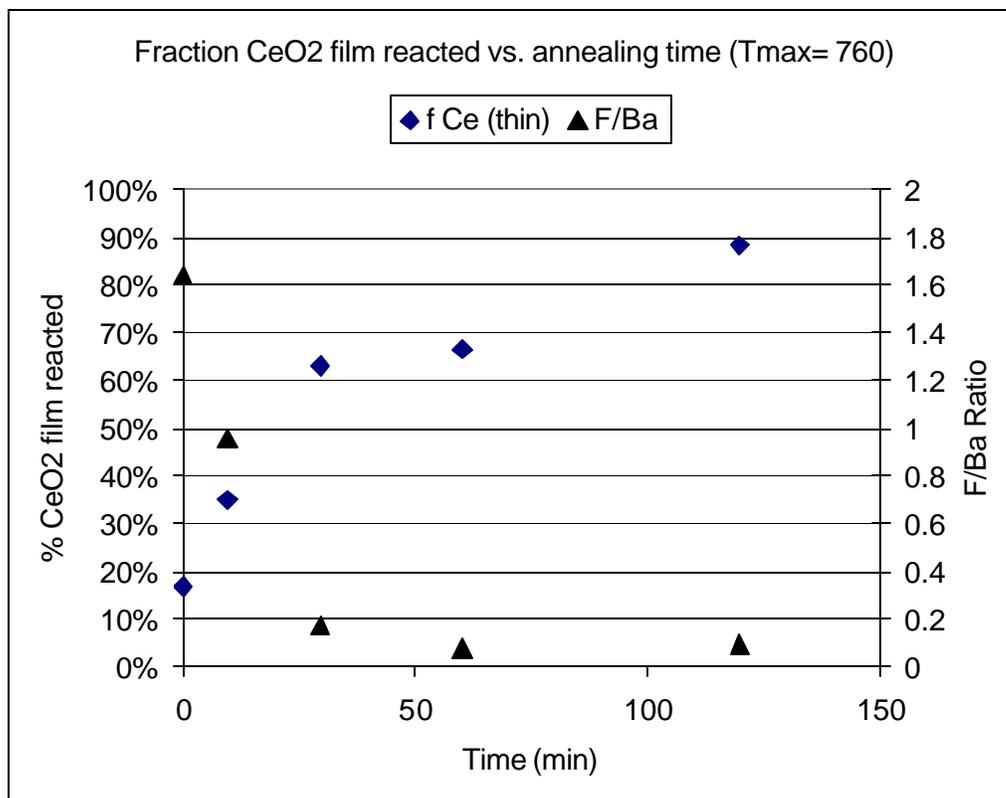


Figure 7. Fraction of CeO<sub>2</sub> film reacted vs. time at 760°C. BaCeO<sub>3</sub> formation follows the parabolic rate law. Almost the entire CeO<sub>2</sub> film becomes BaCeO<sub>3</sub> by the end of processing. Little BaCeO<sub>3</sub> forms during ramping.

### *Summary*

Detailed studies of the physical and chemical changes in MOD-derived YBCO films during processing were performed. XRD and F/Ba ratio measurements were used to establish that MOD-derived films contain significant amounts of yttrium oxyfluoride following decomposition, and that this is most likely  $YF_3$  in solid solution with  $BaF_2$ . A modified Knudsen cell technique was used to determine, for the first time, the actual  $P(HF)$  over ex situ films. This data revealed that reactions in MOD films are significantly more complex than were first assumed. A plausible reaction sequence was determined for MOD-derived films by relating  $P(HF)$  to the free energy of possible reactions.

The combination of F/Ba trajectory and shrinkage trajectory measurements indicates that a fluorine-free liquid phase catalyzes the growth of YBCO. The trajectories indicate that no shrinkage occurs during  $YF_3$  decomposition, and almost no shrinkage occurs during the final conversion of  $BaF_2$  and other precursors to YBCO. The compositional range where significant shrinkage occurs is limited to  $F/Ba=1.8-1.5$ . This acceleration in sintering rate across a narrow compositional boundary is indicative of melt formation across that same boundary. A corresponding increase in sintering rate occurs across a temperature boundary when samples are annealed for 1 hour at a given temperature. A significant jump in shrinkage over a small range in temperature was observed, and the sintering activation energy was lower above the transition temperature. Increased sintering rate across temperature and compositional boundaries is strong evidence of melt formation.

The formation of this melt phase corresponds to the onset of YBCO formation. The melt formation temperature is strongly dependent on processing conditions, so YBCO nucleation can occur over a wide range ( $>60^\circ C$ ) of temperature. The temperature of nucleation, and therefore F/Ba trajectory, impacts the morphology and performance of films. Films processed in an optimal trajectory have high performance; high ramp rate and high moisture conditions yield the same performance as low ramp rate and low  $P(H_2O)$  conditions. Trajectories that remove fluorine at lower temperatures can cross into the melt region at lower temperature. This melt is under-cooled more than a melt that forms at higher temperature, and the corresponding increase in thermodynamic driving force promotes off axis nucleation. Low-fluorine removal trajectories do not have substantial  $a$ -axis grains, but large second phases appear. This suggests second phases grow at elevated temperature and cannot be consumed during the growth of YBCO. Optimum processing avoids both  $a$ -axis nucleation and phase segregation.

BaCeO<sub>3</sub> formation during the annealing of YBCO was quantified using selective etching and ICP. Room temperature 10% HNO<sub>3</sub> dissolves BaCeO<sub>3</sub> and YBCO in minutes while not significantly etching CeO<sub>2</sub> films. ICP can be used to quantifiably detect the amount of Ce ion in solution from areas of film around 0.5cm<sup>2</sup> or larger. XRD is a useful tool for the nondestructive measurement of BaCeO<sub>3</sub> formation, but the peak area measurements must be calibrated to be quantitative. XRD and ICP results show that BaCeO<sub>3</sub> formation follows the parabolic growth law for a layer. Almost the entire ceria cap layer is consumed by the growth of BaCeO<sub>3</sub> after two hours at 760°C, but film performance is not substantially affected. BaCeO<sub>3</sub> growth is substantially slower at 725°C. Very little BaCeO<sub>3</sub> grows during ramping to the annealing temperature.

Budget cutbacks forced significant reductions in time and material devoted to this project in the final year. Work focused on formulating conclusions from the previous quarters. Even so, the project as a whole met nine of ten milestones in a timely fashion.

**Publications:**

- “Trajectory-property relationships in MOD-derived YBCO films”, Physica C, in press (2006).
- “Large-Area Quantification of BaCeO<sub>3</sub> formation during processing of MOD-derived YBCO films”, submitted to Journal of Materials Research
- “F/Ba trajectory- property relationships in MOD-derived YBCO coated conductors”, submitted to IEEE Transactions on Applied Superconductivity (2006).
- “Nitrate-based metalorganic deposition of CeO<sub>2</sub> on yttria-stabilized zirconia.” J. Mater. Res. **21** (1): 1 - 4 (2006)
- “Metalorganic Deposition”, to be published in *Flux Pinning and AC losses in YBCO Coated Conductors*
- “Determination of HF partial pressure during *ex situ* conversion of YBCO precursors.” Physica C **423**: 75–82 (2005).
- “Reactions of oxyfluoride precursors for the preparation of barium yttrium cuprate films”. Physica C **403**: 191-199 (2004).

**Patents: N/A**

**Milestone Status Table :**

ID number	Task/milestone description	Planned completion	Actual completion
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1	Knudsen cell constructed tested with pure BaF <sub>2</sub> to compare with	3/31/2004	3/31/2004
Ba mass loss observed at higher T. Knudsen cell technique proven with YF <sub>3</sub> .			
2	Knudsen cell measurements made on MOD film	3/30/2004	12/31/2003
Direct pHF measurements performed. See Physica C <b>403</b> 191-199 (2004).			
3	Knudsen cell measurements made with e-beam film	3/31/2005	3/31/2005
Measurements did not indicate significant decomposition before 700°C.			
4	Phase identification of transient melt	3/31/2005	3/31/2005
Dramatically enhanced sintering rate occurs at F/Ba ratio ~1.8 -1.5 across a broad range of processing conditions. Melt formation is strongly suspected at this composition.			
5	Trajectory property relationship determined for MOD films	6/30/2005	6/30/2005
Optimum F/Ba trajectory for high J <sub>c</sub> films of all thicknesses (up to 850nm) was found to be the same and characterized by YBCO nucleation ~725°C and F/Ba ratio 1.8. YBCO nucleation is determined by crossing the F/Ba ratio 1.8 threshold, i.e. melt formation. Paper in press.			
6	Trajectory property relationship determined for e-beam films	9/30/2005	
Not pursued due to funding constraints.			
7	Establish protocol for quantitative measurement of reaction with buffer layers	3/31/2006	6/30/2006
Short etches in 10% HNO <sub>3</sub> were used to remove YBCO and BaCeO <sub>3</sub> but not CeO <sub>2</sub> . The amount of Ce ion in solution was used to quantify BaCeO <sub>3</sub> . Paper in press.			
8	Measure degree of reaction in and out of the partial melt zone for MOD films	8/31/2006	6/30/2006
Very little BaCeO <sub>3</sub> formation occurs prior to 725°C during ramping, so little is formed in the melt region. About 25% of a 34nm CeO <sub>2</sub> layer is consumed by BaCeO <sub>3</sub> formation after 2 hours at 725°C.			
9	Measure degrees of reaction in and out of the partial melt zone for e-beam films	8/31/2006	
Partial melt region not identified in e-beam films; not pursued due to budget constraints.			
10	Final report	9/30/2006	

**Budget Data:**

			Approved Spending Plan			Actual Spent to Date		
Phase / Budget Period			DOE Amount	Cost Share	Total	DOE Amount	Cost Share	Total
	From	To						
Year 1	9/1/03	8/31/04	200,000	0	200,000	144,000	0	144,000
Year 2	9/1/04	9/30/05	200,000	0	200,000	269,000	0	269,000
Year 3	10/1/05	8/31/06	115,000	0	115,000	97,000	0	97,000
Totals			515,000	0	515,000	510,000	0	510,000