

Superconductivity for Electric Systems 2006 Project Summary

PROJECT TITLE:	Conversion of oxyfluoride based coated conductors
ORGANIZATION:	Massachusetts Institute of Technology
PRESENTERS:	Michael J. Cima
FY 2006 FUNDING:	\$115,000 of \$200,000

Project Purpose and FY 2006 Objectives: Direct measurements of HF pressure in equilibrium with the film during the BaF₂ process are needed for accurate process design and control. 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. FY 2006 objectives of our project were:

1. Analyze trajectory/property relationships in more detail, especially on e-beam derived films.
2. Develop a protocol for the quantitative measurement of reaction with buffer layers.
3. Measure the degree of reaction in and out of the partial melt zone for MOD/e-beam films.
4. Perform calorimetric studies for relevant reactions in the Ba-Y-Cu-O-F-H₂O system

FY 2006 Performance and FY 2007 Plans: Substantial effort was put forth in FY2006 towards understanding the F/Ba and shrinkage trajectories and their relationship to performance. Preliminary studies indicated fluorine removal at low temperature led to higher performance. 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. The final trajectory tested followed the optimum F/Ba trajectory. The processing conditions, however, used a slow ramp rate (5°C/min) and low water vapor pressure (~0.2 Torr). It was found that this trajectory produced high performance 800 nm films (average $J_c = 1.2 \text{ MA/cm}^2$). This means that trajectory, rather than ramp rate or P(H₂O), controls film performance.

An important discovery in FY 2006 was YBCO nucleation depends of F/Ba ratio. XRD had previously indicated that YBCO nucleation begins around 700°C in high performance films. XRD was performed on films quenched from a high and low fluorine removal trajectory. Both of these trajectories lead to sub-optimal performance, but they have very different chemical pathways. YBCO was detected in the high fluorine removal trajectory at 675°C. YBCO was not found in the low-fluorine removal path until 10 minutes at T_{max} (760°C). Both of these temperatures correspond to a F/Ba ratio of ~1.8 for the respective trajectories. This indicates that YBCO nucleation is dependent on crossing a phase boundary in composition that extends over a wide range of temperatures.

Shrinkage trajectories taken in parallel with the F/Ba trajectories provided compelling evidence for melt formation. The trajectories indicate that no shrinkage occurs during YF₃ decomposition, and almost no shrinkage occurs during the final conversion of BaF₂ 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 indicates 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. The compositional range where shrinkage occurs corresponds to YBCO nucleation, indicating YBCO grows in contact with a fluorine-free melt.

A quantitative technique for measuring BaCeO₃ formation was established in FY 2006, meeting the second goal and thirds goals outlined above. Previous work had focused on detecting Ba depletion in overall film stoichiometry following a selective etch for YBCO over BaCeO₃. 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 HNO₃) was not selective enough for quantitative work. Instead, research revealed that BaCeO₃ dissolves readily in 10% HNO₃, while CeO₂ dissolves much more slowly. ICP was performed to detect Ce ions in solution. A CeO₂ film on YSZ was soaked for 15hrs in 10wt% HNO₃ 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 BaCeO₃ and YBCO both completely dissolve after 10 minutes in 10% HNO₃. Quantitative measurements of BaCeO₃ formation were performed after the selectivity of the

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10% HNO₃ for BaCeO₃ over CeO₂ was established, and these measurements compared to F/Ba trajectories to determine the degree of reaction in and out of the melt region (goal 3 above).

Calorimetric studies were not performed due to budget cuts. There are no plans for FY 2007 as the project has expired.

FY 2006 Results: Shrinkage tests indicate that fluorine removal during BaF₂ conversion to YBCO results in a substantial increase in porosity in MOD-derived films. Also, the ultimate density of thick films is 10-15% less than thin films. Fully processed films are 70-85% of theoretical density.

A number of important trajectory / property relationships were indicated above, including a compositional dependence on shrinkage and YBCO nucleation that indicates YBCO nucleates in contact with a melt phase. The temperature of nucleation, and therefore F/Ba trajectory, impacts the morphology and performance of films. The optimal YBCO nucleation temperature in the 300-800nm films was around 725°C. *a*-axis grains dominated the microstructures of films where YBCO nucleated at <700°C. Large second phases, but no *a*-axis grains, were found when the nucleation temperature was >750°C. 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.

BaCeO₃ formation during the annealing of YBCO was quantified using selective etching and ICP. ICP was found to quantifiably detect the amount of Ce ion in solution from areas of film around 0.5cm² or larger. XRD and ICP results show that BaCeO₃ formation follows the parabolic growth law for a layer, as also reported by NIST in FY 2006. Almost the entire ceria cap layer is consumed by the growth of BaCeO₃ after two hours at 760°C, but film performance is not substantially affected. BaCeO₃ growth is substantially slower at 725°C due to the high activation energy for Ba diffusion in BaCeO₃, calculated to be 8±2? eV/atom. This high activation energy means very little BaCeO₃ grows during ramping to the annealing temperature. BaCeO₃ formation is negligible while in contact with the partial melt region.

Publications:

“Trajectory-property relationships in MOD-derived YBCO films”, submitted.

“Large-Area Quantification of BaCeO₃ formation during processing of MOD-derived YBCO films”, submitted.

“Reaction complexity of TFA-based MOD processing”, submitted to Physica C.

D.E. Wesolowski, M.J. Cima: “Nitrate-based metalorganic deposition of CeO₂ on yttrium-stabilized zirconium” *J. Mater. Res.* 21 (1): 1 - 4 (2006)

“Metalorganic Deposition”, to be published in *Flux Pinning and AC losses in YBCO Coated Conductors*.

M. Yoshizumi, D. Wesolowski, Y. Patta and M. J. Cima. “F/Ba Trajectory-property Relationships in MOD-derived YBCO Coated Conductors.” (Materials Research Society Spring Meeting, Symposium HH: Recent Advances in Superconductivity, San Francisco, CA, 2006) HH2.5.

M. Yoshizumi, D.E. Wesolowski, M. J. Cima: Determination of HF partial pressure during *ex situ* conversion of YBCO precursors. *Physica C* **423** 75–82 (2005).

Research Integration: MIT has collaboration with BNL to address the difference between e-beam derived and MOD derived precursor films. This collaboration has consisted of several face-to-face meetings, many exchanged samples, and measurements being performed at each site. No formal joint experiments have been performed with BNL but significant informal discussion was performed.