STANFORD IN-SITU HIGH RATE YBCO PROCESS: TRANSFER TO METAL TAPES AND PROCESS SCALE UP.

Final Scientific/Technical Report

for Period September 1, 2003 to December 31, 2008.

April 2009

Malcolm R. Beasley

Robert H. Hammond

The Leland Stanford Junior University

Executive Summary

The materials science understanding of high rate low cost processes for Coated Conductor will benefit the application to power utilities for low loss energy transportation and power generation as well for DOD applications. The research in this program investigated several materials processing approaches that are new and original, and are not being investigated elsewhere. This work added to the understanding of the material science of high rate PVD growth of HTSC YBCO assisted by a liquid phase.

A new process discovered uses amorphous glassy precursors which can be made at high rate under flexible conditions of temperature and oxygen, and later brought to conditions of oxygen partial pressure and temperature for rapid conversion to YBCO superconductor. Good critical current densities were found, but further effort is needed to optimize the vortex pinning using known artificial inclusions.

A new discovery of the physics and materials science of vortex pinning in the HTSC system using Sm in place of Y came at growth at unusually low oxygen pressure resulting in clusters of a low or non superconducting phase within the nominal high temperature phase. The driving force for this during growth is new physics, perhaps due to the low oxygen. This has the potential for high current in large magnetic fields at low cost, applicable to motors, generators and transformers.

The technical demands of this project were the motivation for the development of instrumentation that could be essential to eventual process scale up. These include atomic absorption based on tunable diode lasers for remote monitoring and control of evaporation sources (developed under DARPA support), and the utility of Fourier Transform Infrared Reflectivity (FTIR) for aid in the synthesis of complex thin film materials (purchased by a DURIP-AFOSR grant).

Executive Summary

The materials science understanding of high rate low cost processes for Coated Conductor will benefit the application to power utilities for low loss energy transportation and power generation as well for DOD applications. The research in this program investigated several materials processing approaches that are new and original, and are not being investigated elsewhere. This work added to the understanding of the material science of high rate PVD growth of HTSC YBCO assisted by a liquid phase.

A new process discovered uses amorphous glassy precursors which can be made at high rate under flexible conditions of temperature and oxygen, and later brought to conditions of oxygen partial pressure and temperature for rapid conversion to YBCO superconductor. Good critical current densities were found, but further effort is needed to optimize the vortex pinning using known artificial inclusions.

A new discovery of the physics and materials science of vortex pinning in the HTSC system using Sm in place of Y came at growth at unusually low oxygen pressure resulting in clusters of a low or non superconducting phase within the nominal high temperature phase. The driving force for this during growth is new physics, perhaps due to the low oxygen. This has the potential for high current in large magnetic fields at low cost, applicable to motors, generators and transformers.

The technical demands of this project were the motivation for the development of instrumentation that could be essential to eventual process scale up. These include atomic absorption based on tunable diode lasers for remote monitoring and control of evaporation sources (developed under DARPA support), and the utility of Fourier Transform Infrared Reflectivity (FTIR) for aid in the synthesis of complex thin film materials (purchased by a DURIP-AFOSR grant).

A. <u>Project Objective</u>:

The objective was to understand and develop the Stanford high-rate electron-beam deposition process. The process is capable in principle of meeting the cost/performance (C/P ratio) requirement of $10/kA-m desired for Coated Conductors (CC), and if the process can be scaled up, a realistic goal for this process is a C/P ratio of $1/kA-m. The research was aimed at optimizing the potential of the approach and characterizing the process requirements and to explore scale-up Issues in collaboration with Los Alamos National Laboratory. This task was concerned with determining the optimal deposition temperature and oxygen activity for a given deposition rate in the Stanford chamber, and then

assist the effort at LANL in transferring the Stanford Process to the system at LANL. Originally conceived as a in-situ co-evaporation process using atomic oxygen, it evolved into a two step process using a low temperature amorphous precursor made in the same multi-source high rate equipment, followed by a anneal step at a certain higher temperature in oxygen. This change was made in part because of the difficulty in scale-up of the atomic oxygen requirements at LANL, and partially because of the simplicity and low cost of the high rate liquid assisted precursor process developed in this program. The Stanford program until recently was concentrated with demonstrating this process in YBCO. This was successfully done, achieving greater than 1 MA/cm2 in a 1.2 micron film made at a rate greater than 100 Å /sec. The next step would have been to improve the critical current using the types of defects or artificial pinning centers being used in the CC field. However at this point it had been recognized by many in the CC field that these methods may have reached the limit using these methods. At the same time a new development using the Rare Earth elements Sm and Nd (which have a solid solution involving the Ba) had demonstrated a new mechanism for pinning based on what we call "Composition Clustering". Since this fits nicely into the Stanford process developed for YBCO the attention evolved to the study of SmBaCuO (Sm123 in this report). In the last year the limited research support available was drawn to an accidental discovery—"Anti-site Disorder Clustering"—found when growing Sm123 at low oxygen pressure. These clusters have the potential for strong vortex pinning in high magnetic fields. When combined with high rate deposition the cost / performance ratio could be very low, combined with superior high field critical current.

History of collaboration with LANL and ORNL: Since the Stanford project was intended to be research resulting in scale up of a Coated Conductor process, particularly at LANL, the history of this collaboration is outlined:

1. Initial effort was with 3M as part of a CRADA between ORNL, LANL, 3M and Stanford U. Stanford's effort was then directed towards using atomic oxygen for *in situ* growth of YBCO at high rates. 3M's effort was mainly directed towards setting up the tunable diode laser-AA rate control of Ba and Y, heating of tapes, and experiments for generating atomic oxygen. 3M provided compositional data to Stanford using ICP (inductively coupled plasma spectroscopy) and other characterization data (SIMS, AUGER.)

2. 3M's research effort was stopped in 2003 and the research of PI Jonathan Storer moved to LANL along with the equipment. There was a year delay in starting up at LANL.

3. LANL effort led by Storer to scale up the Stanford work was not able to get conditions suitable for *in situ* growth: atomic oxygen delivery to the substrate was not characterized because atomic oxygen monitor was far upstream from the substrate

4. Stanford switched to precursor two-step process. Initially this required rapid addition of oxygen while sources were hot. This was a major procedural problem

at LANL that was never overcome (because this oxygenated the large Cu ingot and made it unusable unless time consuming degassing was used), and so the Stanford results were not repeated sufficiently. It was later found that Stanford could make precursor at room temperature and at 10^{-5} torr, unfortunately too late to be implemented at LANL.

5. Collaboration continued in 2006 between Stanford, LANL and ORNL on the two-step process where ORNL led by David Christen reproduced the Stanford results, making the F-free precursors by PLD and obtained good results considering artificial pinning centers were not pursued.

Introduction

Key to the successful application of high-temperature superconductivity to electric power systems is the development of a suitable high-current conductor. The DoE Coated Conductor Program is aimed at exploiting the potentially superior properties of YBCO and RE-BCO for such applications. As is well known, to manufacture coated conductors in an economical fashion will require a high-rate deposition process. One candidate for this process is the high-rate electron-beam deposition process developed in our group at Stanford. Specifically, the process is capable in principle of meeting the cost/performance (C/P ratio) requirement of $10/kA-m desired for coated conductors, if the process can be scaled up to large areas and the needed material performance can be achieved reliably at the desired high rates and relatively thick conductors. Indeed, a realistic goal for this process is a C/P ratio of $1/kA-m, at a deposition rate of 300 to 600 Å/sec. Such performance could lead to a commercial process and would satisfy all the objectives of the solicitation to which this proposal is directed.

The goals in original proposal evolved to the following:
- Explore high performance coated conductor to satisfy applications at high magnetic fields
- Explore the material science of processes that would be high rate and low cost.

B. Motivation:

Recent surveys set the agenda for future requirements for Coated Conductors market entry in the power grid:

- BES--DOE Workshop Report on Superconductivity Performance Needed vs. Present Performance.
- Market Readiness (Navigant) Cost, Cost / Performance.

In brief, the performance requirements needed are roughly a factor of 10, compared to current values:

- x 10 higher in performance.
- x 10 lower in cost.

The Market Readiness Review (Navigant) was commissioned by the Office of Electricity Delivery and Energy Reliability to investigate the requirements of HTSC applications and the market readiness. The review summarizes the requirements of various utility applications in terms of performance and Cost-to-Performance ratio, C/P. The C/P ratio will be our focus. Our aim is to develop a process with low C/P, approaching $ 10 to $ 1 / kA-m. The present processes being developed predict at best to approach $ 50/kA-m.

  To appreciate the meaning of the C/P metric, we show in Fig. 1 its derivation in terms of parameters of processing of tape shaped Coated Conductor (which includes all present approaches). This directly applies to a one step process, but can also be applied to a multiple step process where the rate limiting step determines the C/P for the whole process. The important result of the final expression is that the rate R of the process (the deposition rate or the conversion rate) times the area of the material being processed need to be large. The performance is generally taken as the critical current, I_c, either as the self-field I_c, or at the operating field and temperature, $I_c(H,T)$. The thickness t_s of the superconductor cancels out, leaving the apparent performance as the critical current density, J_c. This is often confusing, as the total current or current per unit of width is usually required as a specification. Thus the current/width (amps per cm width) is usually a separate specification.

$$\text{Cost / Performance} = \frac{\text{Cost / Year}}{(\text{Tape length / Year}) \times \text{Performance}}$$

1. Cost---total cost of capital, depreciation +material, labor, etc.

2. Length of tape/ year = y S $\qquad S = L \times \dfrac{1}{T_p} \times n$

$$= \frac{L \times R \times p \times n}{t_s} \ [\text{meter / sec}]$$

Note: for process specific $\qquad L \times R/(t_s / p)$

3. Performance = current : I

$$C/P = \frac{\$ \, \text{Cost}}{\dfrac{L \times R \times p \times n}{t_s} \times I}$$

$$I = I_c = J_c \times w_t \times t_s, \boxed{C/P = \frac{\$}{R \times L \times W \times J_c}}$$

$$[\, \$ / \text{kA-m} \,]$$

S = Speed of Process
y = Fraction Yield
n = # Post process slitting
L = Length of Process
T_p = Time of Process per Pass
p = # Passes through Process
R = Rate (Thickness/Time)
t_s = Total Thickness of supercond after p Passes
w_t = Tape Width
W = Width of Process
e = Engineering Fraction

Figure 1. Derivation of Cost / Performance metric.

C. Summary of Stanford Process

The left chart in Figure 2 shows the region in temperature and oxygen partial pressure where the YBCO is stable. This YBCO stability diagram is the basis of our efforts and is used throughout this report to describe our efforts. The nearly vertical line through the stable region shows the position in temperature, oxygen pressure where the liquid $BaCu_2O_2$ (called 012 hereafter) undergoes a transition to two solids, CuO and $BaCuO_2$. Thus the liquid region overlaps the YBCO stability region on the left side of the line (shown hatched). The figure on the right shows the phase diagram for YBCO in equilibrium with the compounds shown, in the region to the left of the line, i.e., the liquid region. This is a conjectured phase relationship base on our observations, and needs further confirmation. A major departure from the published equilibrium diagram is the absence of tie lines to the 211 compound when the total composition is slightly Ba poor, as indicated by the red dot. This is the region in which our work is located.
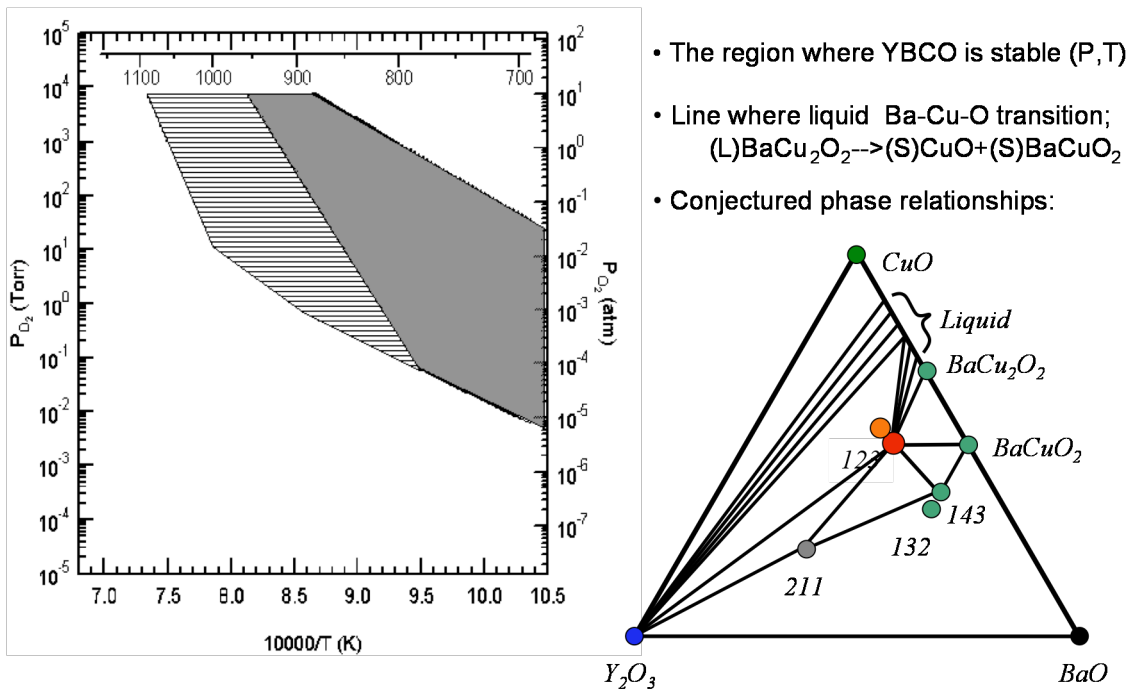
Figure 2. YBCO stability and phase diagrams.

Initial Efforts:

The initial effort was to deposit directly into the hatched region with the assistance of activated oxygen. This required a high flux of atomic oxygen in our approach (other forms of activated oxygen could be used). This approach showed signs of success until the monitor of the atomic flux failed and we were not able at that time to replace it. Without this monitor it was not feasible to repeat the success with consistency. Furthermore during his period the characterization facility (in particular the XRD) we depended on was ineffective due to staffing problems. However we found success if the substrate heating was turned off and the oxygen pressure increased suddenly after the sources were turned off. We found this scheme still successful even as the atomic oxygen source was not used. The success was rationalized as being due to a source of atomic oxygen generated at the surface of the Ba and Y by a known process called Electron Stimulated Dissociation of the Metal Oxides. Without the monitor this could not be checked. The necessity of the rapid rise in the oxygen was ascribed to the need to get the deposit into the stable region before it could decompose.

A turning point was the installation of a FTIR (Fourier Transform Infrared Reflectivity) spectrometer onto the growth chamber. This was originally for the remote measurement of substrate temperature, based on the radiation spectrum. This was successful, but more information was evident as the sample responded

8

to the changes in oxygen and temperature. The adsorption and reflection (as a function of the wavelength) showed unexpected detail that eventually lead to a new interpretation of the process. Since this was a critical turning point in the research we devote a careful discussion of the meaning of the FTIR measurements in the next section.

D. Meaning of FTIR Measurements:

The stability boundary we are concerned with (near 850 C) is described by the invariant reaction:

$$7(123) = 3(211) + \text{"132"}O_{6+y} + 8(012) + (5-y)/2 \; O_2$$

In Figure 2 this stability boundary is on the left side of the hatched area. At the high temperature side (left) the phases are those on the right side of the equation above, in bulk equilibrium. At constant temperature the oxygen pressure drives the reaction to the left, i.e., to grow YBCO from the mixture of 211 and 132 in a liquid 012. Note that we never see 211, and we suspect that Y2O3 forms instead of 211 when there is an interface present.

It is useful in the following discussion to note that in the equation on the right side above over 3/4 of the Cu ions make up the liquid 012, i.e., the liquid is the major part of the mixture.

Consider now the sequence of events following the deposition of the atoms of Y, Ba, and Cu, along with oxygen, on the substrate at a temperature of 830 C:

1. At the deposition pressure of 5×10^{-5} Torr oxygen, Y_2O_3, BaO, and CuO_x are probably formed in a loose mixture. When the temperature is lowered and the sample removed at this stage it appears as a powder that quickly reacts with the moisture in the lab air. XRD shows no structure. XPS is difficult to perform on this mixture, but the Cu seems to have a valance state of +1. During the deposition the FTIR shows an interference pattern of low amplitude indicative of a growing film only partly transparent as shown in Figure 3, indicated at the far right of the figure, during the start of deposition. The interference maximum wavelength (in units of cm^{-1}) changes as the film gets thicker.
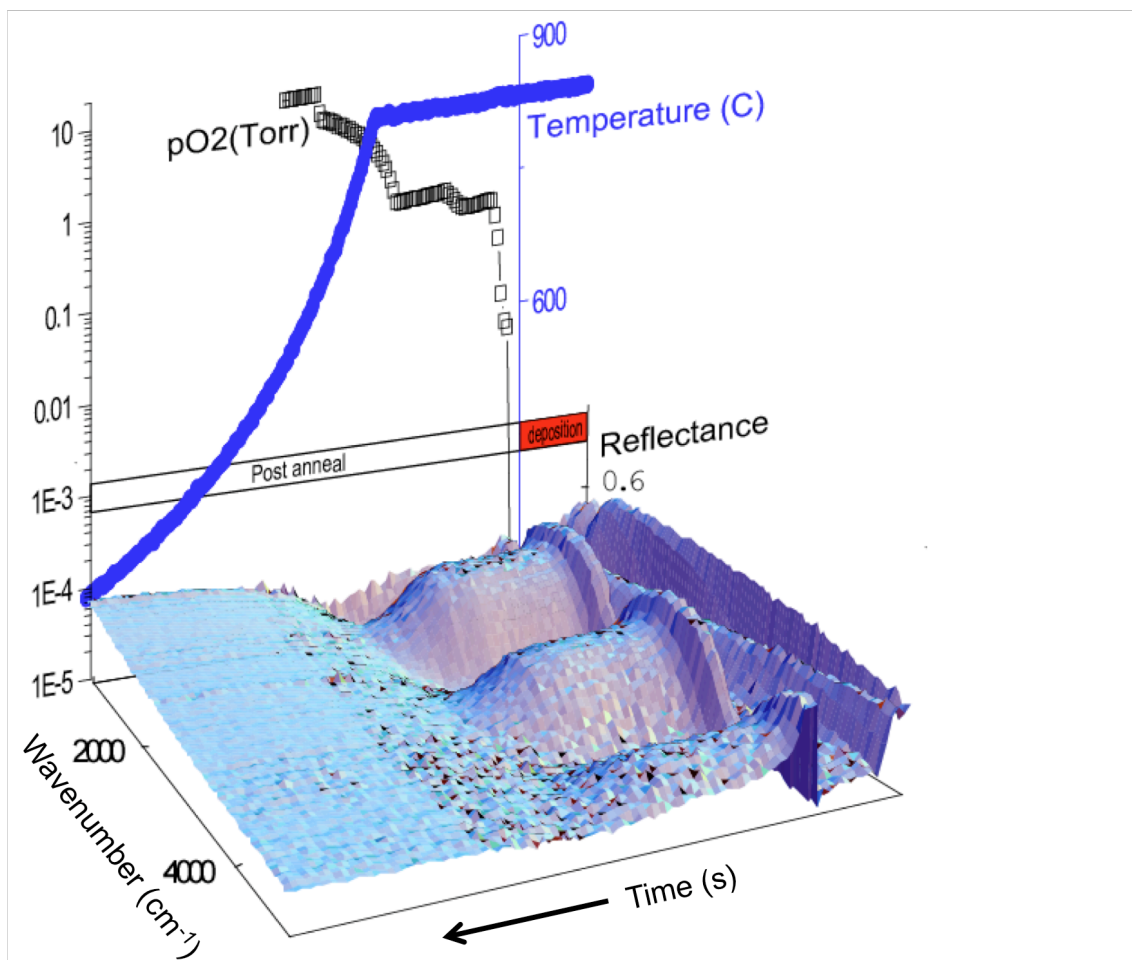
Figure 3. FTIR during deposition and oxygenation. See text for details

2. As the oxygen pressure is raised to about 10^{-3} Torr there is a sudden large increase in the transparency resulting in the FTIR interference amplitude increase as shown in Fig. 3. The index of refraction is about 2. When cooled and removed to air it is fairly stable, and appears transparent. Fig. 4 is the FTIR response if the sample is cooled in 3 mTorr showing that the "glass" state is maintained to room temperature – this is discussed later in connection with precursor preparation. XRD shows a small amount of some unresolved phases. XPS shows Cu valence of +1. (It would be interesting to have Raman data on this material, perhaps to show the bonding among the atoms of this "glass", perhaps to show that the "glass" formation is a change in the bonding-structure at short range.) As discussed below, when only the 012 is deposited the same behavior in the FTIR at these stages are seen. It is therefore tempting to assign the FTIR behavior entirely to the liquid or glassy 012.
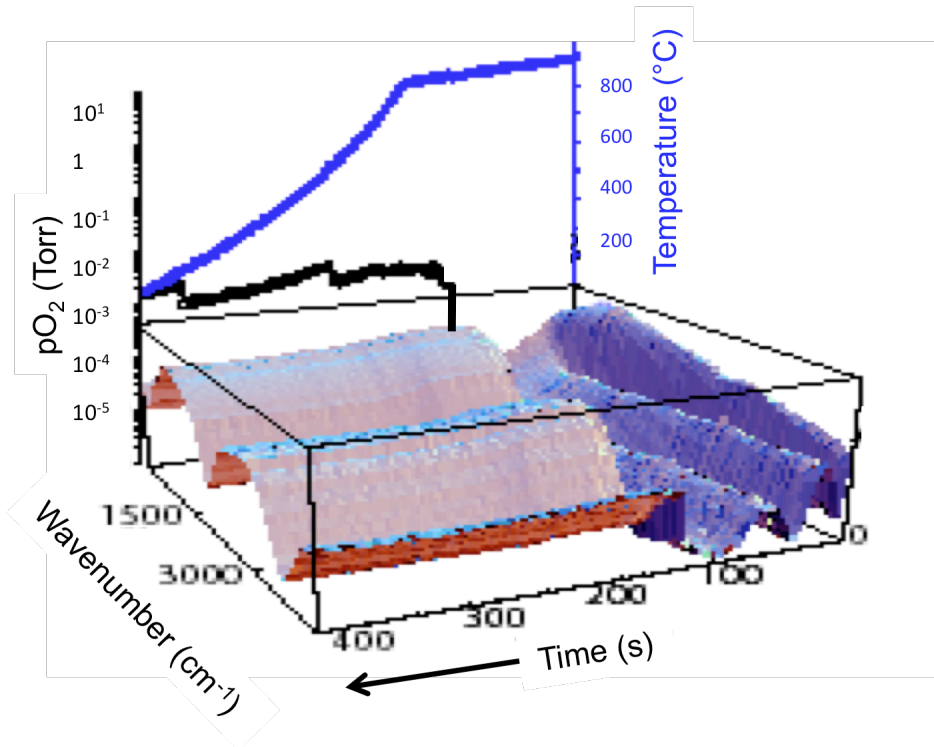
Figure 4. FTIR of YBCO deposited at 830°C, 5×10^{-5} Torr O_2, then oxygenated to 3mTorr, then cooled to room temperature. Note no change in response during cooling.

3. When the oxygen is increased to the region where YBCO is stable (0.2 Torr at 830 C) the FTIR shows a sudden decrease of about 10 % in amplitude shown in Figure 3. Based on XRD in the Dome (a temperature and gas controlled stage attached to the XRD facility) while traversing this same path, there is no structure till the YBCO stable region, where YBCO growth starts. Thus the decrease in the FTIR seems to indicate the growth of the YBCO.

4. As the oxygen is increased there is no apparent further change in the FTIR when in the liquid 012 region, as far as is known now. It will be interesting to follow the possible changes as the growth rate is changed in different parts of the stability region, and outside of it. This would be extremely interesting, as the growth mode appears to be different in the chamber, where we have no monitor of growth, compared to the Dome. The FTIR measurements have mostly been done using an LANL IBAD-MgO with a cap of LMO or CeO2 (this substrate was used because it remained flat and gave a good reflection). Growth on IBAD has not been good, possibility due to particles. The growth of interest is on RABITS, and this should be used to see if FTIR could resolve the details of the growth modes of interest (RABiTS has been the substrate used for most of the work described in this report).

5. Decreasing the temperature and then increasing the oxygen changes the $YBCO_6$ insulator into a $YBCO_7$ metal. This is seen by the FTIR first showing a decrease in transparency followed by an increase in reflectivity and metallic Drude behavior shown in Figure 3.
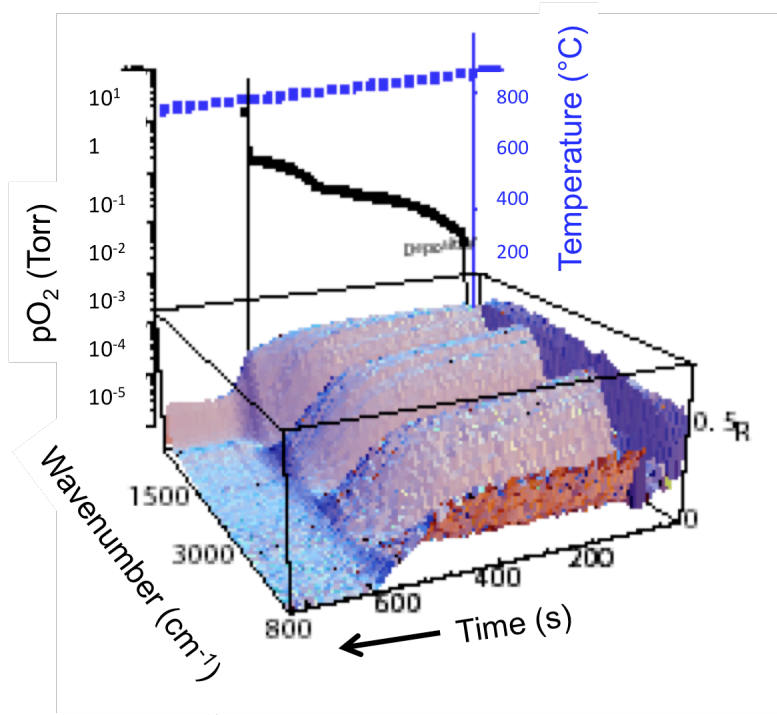

Figure 5. FTIR during deposition of $BaCu_2O_3$, followed by oxygenation to 3mTorr. Then additional O_2 to cross liquid to solid decomposition line.
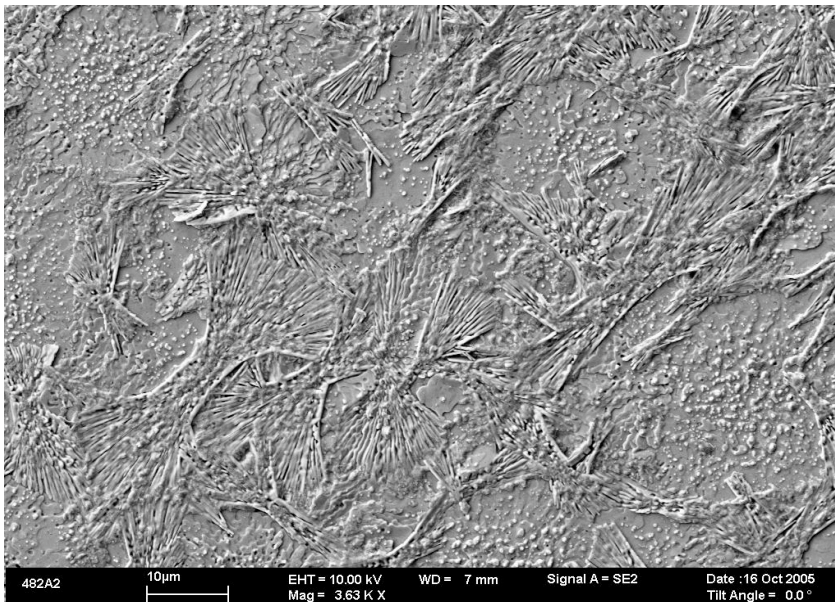

12

Figure 6. SEM of sample 482A2 surface, showing results of decomposition of liquid to solid

Above it was noted that the behavior of the FTIR is mainly due to the 012,($BaCu_2O_2$). Fig. 5 shows the FTIR when only 012 is deposited at 830°C in an oxygen pressure of $5x10^{-5}$ Torr. the same conditions as when depositing YBCO discussed above. The same path of increasing oxygen while keeping the temperature at 830°C is used. Note that at about $3 x10^{-3}$ Torr there is the same sudden jump in the FTIR amplitude, as seen with the YBCO deposition. Increasing the pressure of oxygen through the stable region of YBCO results in no change in the FTIR---while in the above case with YBCO deposition there was a decrease at 0.2 Torr, where the YBCO started growth.

At the pressure of about 1 Torr there is a sudden loss of transparency. This is the point where the liquid transforms to the two solids, CuO + $BaCuO_2$. Fig 6 shows the surface of an YBCO growth in the liquid after it has transformed, showing the dendritic growth characteristic of the decomposition on the surface. Unexplained so far is the gradual decrease in the transparency earlier at lower pressure at long wavelengths (short wave numbers).

Fig, 7 shows the path discussed above as Path 1. Path 2 gave a different, and interesting, FTIR behavior: The same result is observed in the FTIR up to the change in direction (stopping the increase in oxygen), and cooling in a pressure of 3 Torr. However there was no indication of a phase change until the temperature reached lower than 650°C, where the amplitude suddenly decreased by half. This needs further investigation ---tentatively it may be due to the liquid supercooling to that point, then freezing to remain the glass-amorphous 012.
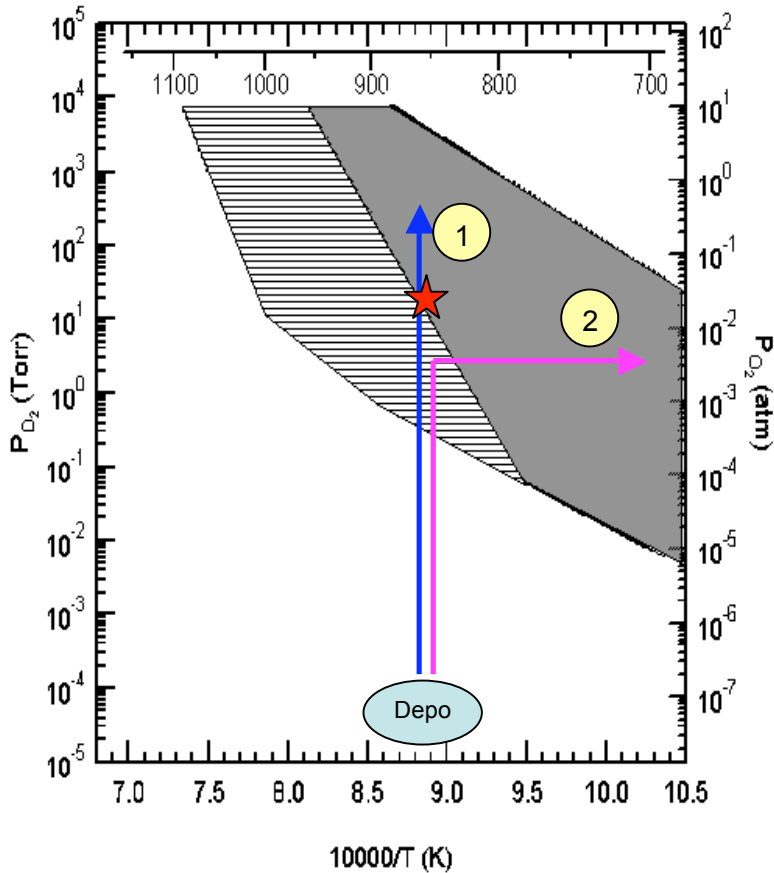
Figure 7. Paths in oxygenation of 012: Path 1 shown in Fig.5, Path 2 discussed in text

In all of the Dome experiments discussed later we have needed a so-called precursor, which was prepared in the evaporator and then cooled and removed to the Dome. The question of possible changes in this process is partially answered by the following experiments using the FTIR:

In Fig 4 YBCO is deposited at nominal conditions, 830°C and $5x10^{-5}$ Torr, oxygen brought up to $3 x10^{-3}$ Torr, then the temperature decreased to room temperature. Note that there is no change in the FTIR during the cooling. This implies that the "glassy" state is maintained.

Similarly, in Fig. 8 YBCO is shown deposited at 300°C in $5x10^{-5}$ Torr. This mimics the precursors made for the Dome for the heating in fixed oxygen concentrations. Note that the growing film is already at large FTIR amplitude under these conditions, at the low pressure of $5x10^{-5}$ Torr. This supports the observation that the thermodynamics seem to predict a lower oxygen pressure at lower temperature for all of the reactions, including the transformation to the "glassy" state. Does this suggest that the "glassy" state is a thermodynamic state, and not kinetically determined? If kinetics determines the formation at 830°C, it
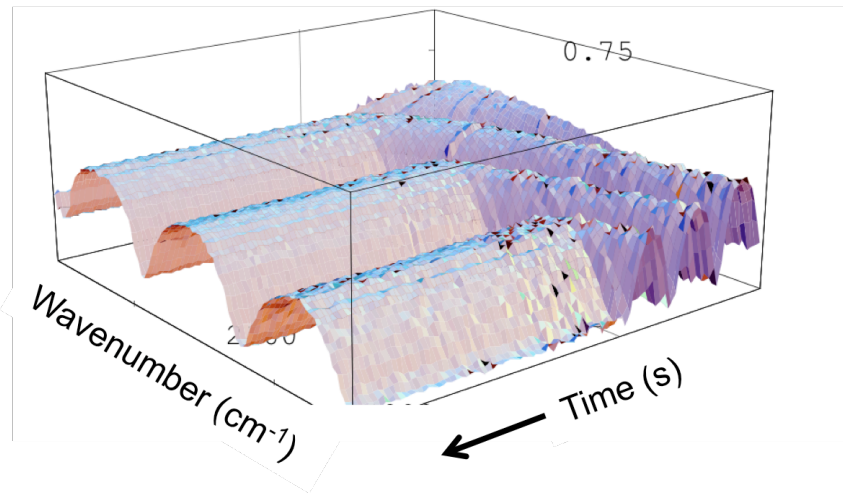
14

Figure 8. FTIR for YBCO deposited at 300˚C, 5x10^{-5} Torr oxygen showing full fringe amplitude of the "glass" state during deposition.

should take place at a lower oxygen pressure? Repeating this experiment at 300˚C and a lower oxygen pressure, followed by adding oxygen, the FTIR could show the occurrence of the change to the "glass" state. Repeating at higher temperatures could produce a map of the "glass" state in P vs. T.

The FTIR results above answer many questions concerning the stages leading up to the growth of YBCO in its stable region, but also many questions remain, and further investigations are suggested. One was pointed out above regarding using the FTIR to obtain more detailed information on the different growth modes that are the greatest concern now. As pointed out in later sections the YBCO growth morphology can be perfect "c" axis, "c" plus "a", varying amounts of polycrystalline (showing 103), or fully polycrystalline. The origin and cause of the different morphologies are now only based on conjecture from post-deposition empirical evidence of many experiments and attempts. An in-situ monitor of the morphology and when they occur is needed (the XRD-Dome has provided very good insights, but for some unknown reason the processing in the Dome at present is different from that in the evaporation chamber). The signature in the FTIR may be too subtle to see, but it is worth considering given the importance. Until better IBAD substrates are available this would have to be done on RABITS and conducting crystals.

With the new prospective furnished by the FTIR measurements during the transit in oxygen pressure and temperature a new process became possible, making use of precursors.

E. Key Discovery---Precursor Approach to Growth:

As an alternative to forming the YBCO phase during deposition in the region of the stability diagram where it is stable, we have found (above) that precursors can be deposited as "glassy" amorphous mixtures of the atoms in other regions of T and oxygen pressure, and then brought to the stable region in oxygen and temperature where the crystal phase grows. If the region includes the liquid $BaCu_2O_2$ the growth is very rapid---say in seconds.
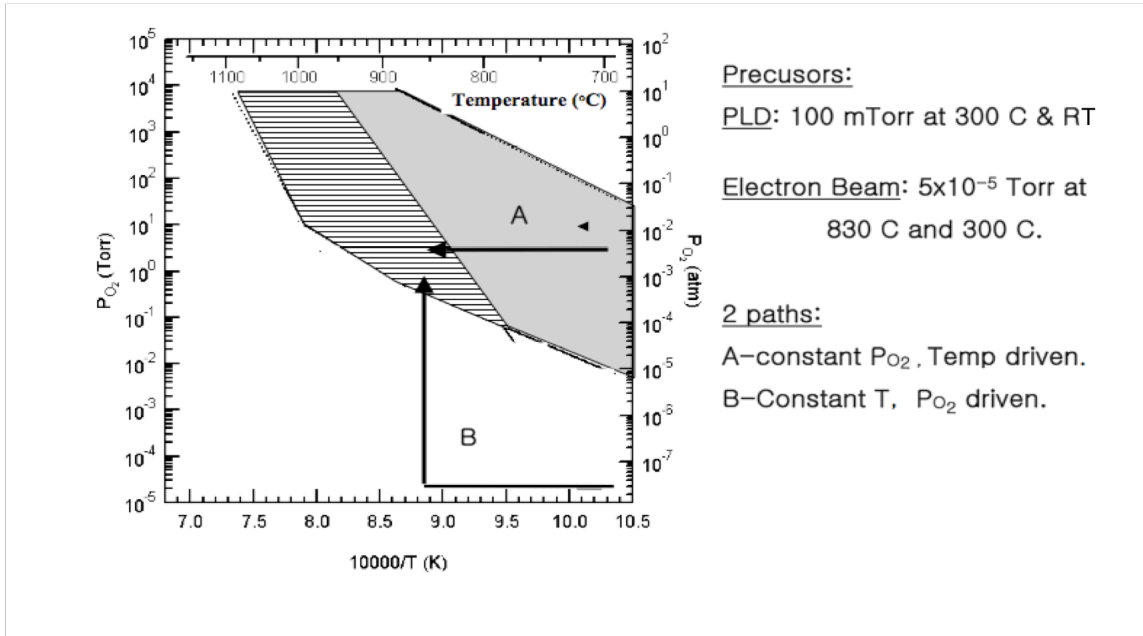
Precursor Paths to Reaction Explored:

Figure 9: Precursor Paths Explored

a). **Precursor deposition**: Precursors (which are found to be an amorphous-glassy mixture) are made in a variety of ways and parameters:

1. PLD at 100 mTorr oxygen partial pressure, at room temperature and 300 C.

2. Electron Beam evaporation at 5×10^{-5} Torr, at 800 C, 300 C, and room temperature.

b). **Precursor is reacted** to form crystalline YBCO when the temperature and oxygen pressure are brought into the overlap of the YBCO stability region and the region of liquid 012 ($BaCu_2O_2$). Fig 9 shows the YBCO stability region bounded by the solid lines, and the overlap with the region of liquid 012 ($BaCu_2O_2$) indicated in the hatched region, ending at a line which separates the liquid 012 and the 2-solid decomposition products. This region can be accessed via many paths in T, $P(O_2)$ from low temperature (even room temperature)

ranging to high temperature (~830 C). and 10^{-5} Torr O_2, which makes the process flexible: The precursor can be cooled to room temperature, and then reacted as when made at room temperature:

i). Heat in low $P(O_2)$ (< 10^{-4} Torr.) to about 830 C, then increase the $P(O_2)$ to the stable region (nominally 1 Torr). This is shown as Path B in Fig. 9.

ii). Heat at $P(O_2)$ ~ 1 Torr, till 830 C (Path A), or
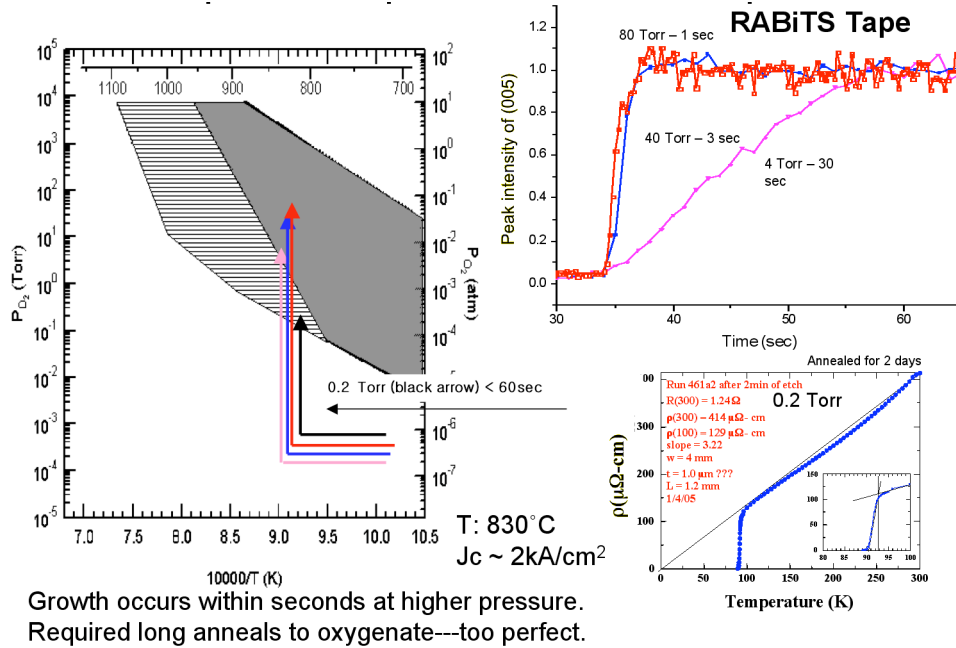
iii). Some combination of these paths.

Figure 10. Traces of temperature and pressure using the Dome experiment.

This key result is summarized in Fig. 10. In these XRD-Dome runs the precursor was again installed in the Dome as before, but the path used was Path B in Fig. 9, where the heating was in argon (no oxygen) until the desired temperature was reached (here 830°C) and then the oxygen-argon mixture was flushed through the dome. The top right panel shows the XRD intensity of the 005 peak as a function of time for various oxygen final partial pressures indicated by the tip of arrow in the figure. Because the oxygen partial pressure was measured external to the dome and there was a time delay for the for the mixture to push through the dome and the lines connecting to the oxygen analyzer-sensor, the actual time for the oxygen to reach and displace the argon in the dome is not known. The higher pressures show a faster rise of the 005 and thus the growth of the YBCO---in about a sec for the highest pressure----however it is suspected that the growth occurs during the transit in pressure through the stable region, and the final pressure may not indicate the point where the highest rate of growth is. This

17

remains an uncertainty until further measurements are done. In this case and other cases where the growth occurred above the liquid line the morphology tended to be polycrystalline and "a" axis in different amounts mixed with the c-axis. The fastest growth in this figure however was perfect c-axis, even though it and the others were grown on RABiTS tape supplied by American Superconductor Corp. The lower right panel shows the $\rho(T)$ after 2 days of oxygen anneal for the film reacted at 0.2 Torr oxygen, indicated in the left panel.

Summary of discoveries:

- Glassy precursor seems special.
- Found conversion rate very high in liquid assist region.
- But generally morphology is too "perfect". Need pinning centers for high current density.

Need for Pinning:

- How to induce pinning?   There are generally divided into:
  - defects introduced during growth, and
  - artificially introduced pinning centers.

Defects during growth include columnar growth found when deposition is below the liquid assisted region, where low surface mobility favors island nucleation. Another form of defect we have seen at high rate in the liquid assisted region when apparently supersaturation nucleation can occur when the temperature and oxygen pressure is rapidly swept through the stable region. J_c values of 5 MA/cm^2 were measured, and TEM showed island growth. However, it was judged to be enough non-reproducible to be considered for a process.
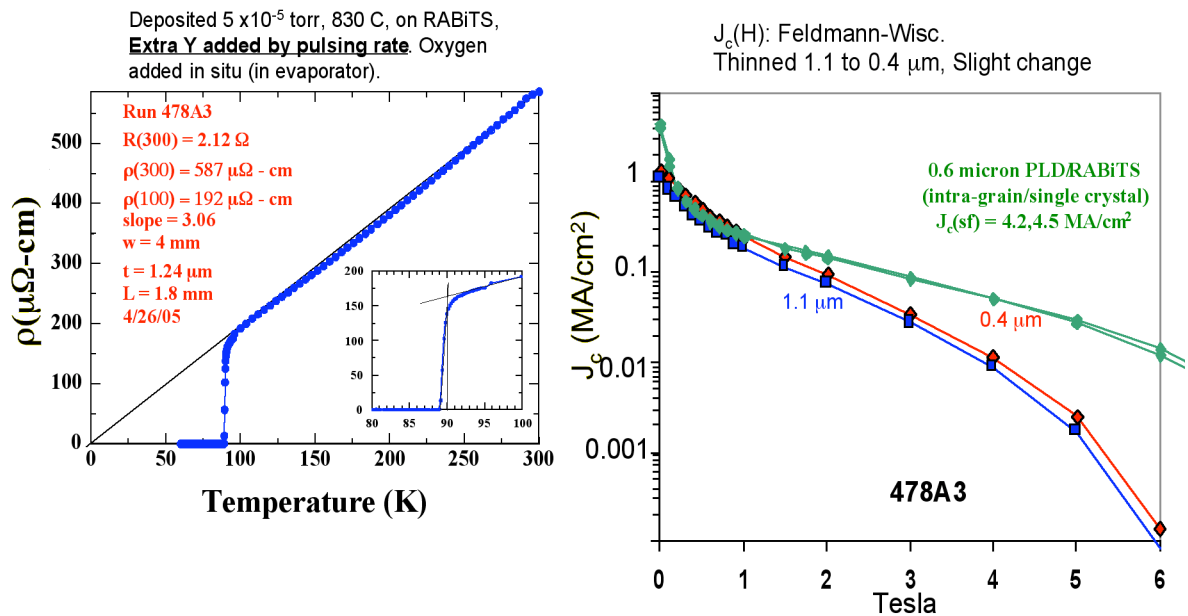
Artificial Pinning Centers (APC):

Some of the APC in use include:

- Y_2O_3 particles by adding extra Y to the deposition.
- 211 layer/particles.
- Rare-earth oxide particles.
- $BaZrO_3$ and BaSnO3 particles by addition to the deposition flux.
- Clustering of lower T_c regions by composition clustering in solid solutions of Nd and Sm 123.
  - Studied in bulk, the "peak effect": Sang-Im Yoo, M. Murakami et al.
  - Studied in Sm PLD films: Y. Yoshida, M. Miura et al (Nagoya), K. Matsumoto (Kyoto).

Y_2O_3 particles:

Due to limited resources only Y_2O_3 was considered. We were successful in incorporating defects in the otherwise perfect growth discussed above by increasing the Y content during the precursor growth. The Y rate was pulsed

18

once every second by decreasing the size of the deflected electron beam, resulting in a sudden pulse of Y rate. The defected growth now was easy to oxygenate, and the results are shown in fig. 11. The TEM showed two-dimensional growth of Y_2O_3 (Fig 12). The Jc(SF) is ~ 1.2 MA/cm2. The Jc(H,77K) is shown in Fig 11, and is compared to a PLD 0.6 micron film. The film was 1.1 micron thick originally, then was etched to 0.4 micron and re-measured. The fact that there was no thickness dependence in this range of thickness is evidence that the pinning is homogeniously distributed through the thickness, consistent with the TEM observations as shown Fig 12. This is a very encouraging result, meaning that the Jc is independent of thickness, and thus large total currents are possible by going to thick films.

Deposited 5 x10^{-5} torr, 830 C, on RABiTS, **Extra Y added by pulsing rate**. Oxygen added in situ (in evaporator).

Run 478A3
R(300) = 2.12 Ω
ρ(300) = 587 μΩ - cm
ρ(100) = 192 μΩ - cm
slope = 3.06
w = 4 mm
t = 1.24 μm
L = 1.8 mm
4/26/05

J_c(H): Feldmann-Wisc. Thinned 1.1 to 0.4 μm, Slight change

0.6 micron PLD/RABiTS (intra-grain/single crystal) J_c(sf) = 4.2,4.5 MA/cm²

1.1 μm
0.4 μm

478A3

Note: No thickness dependence 1.1 – 0.4 μm
Suggests laminar growth grain structure, liquid phase involved
Comparable with 0.6 μm PLD with J_c(sf) = 4.2 MA/cm².
Oxygen added to chains easily--i.e., defects in growth.

Fig. 11. Electron beam deposited on RABiTS at 100 A/sec, in glassy state. Reacted in-situ at 830 C, 1 Torr of oxygen. Y_2O_3 added by pulsing the Y rate during forming the precursor. Pinning by Y_2O_3 particles and plate-shaped regions.

In addition to this precursor discovery being important materials science, there is an important technological aspect. This allows a new process in which the preparation of the precursor is made at say room temperature and in a

convenient oxygen pressure without careful control of the instantaneous composition, temperature and oxygen pressure. The deposition means can be a number of possible high rate, large area processes (such as electron beam evaporation, plasma flash evaporation, etc.). The reaction step can be an inline tube furnace, a Rapid Thermal Annealing (RTA) setup, or heating of the metal tape by passing a current through it, all in a region of oxygen partial pressure. Since the reaction appears to be very rapid, this would not be a limiting step.

The YBCO effort above constituted the PhD thesis of Jeong-Uk Huh. When the post-doc Dr. Akio Tsukada arrived in April 2007 the decision was made to replace Y with Sm to explore the expected beneficial properties, as discussed below.
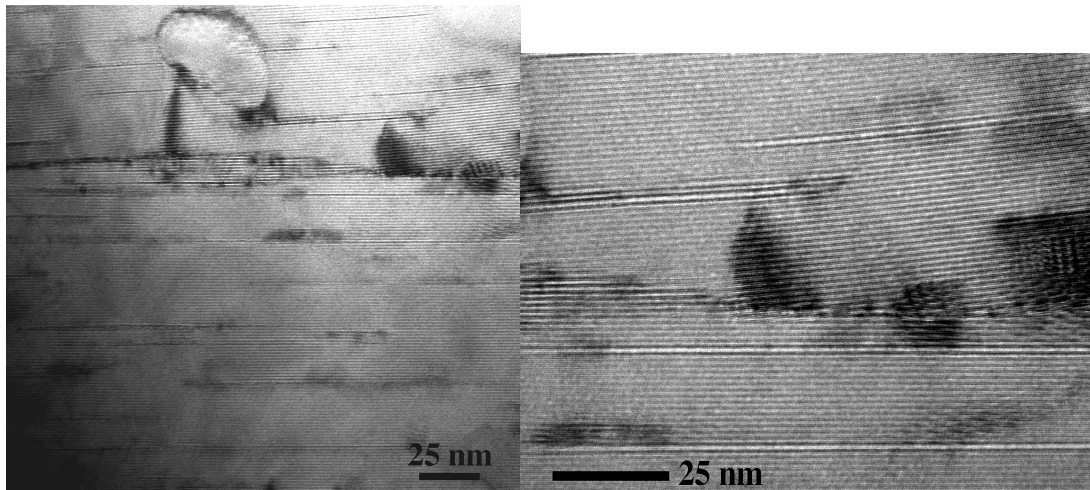

Figure 12. TEM cross sections showing Y_2O_3 2-dimensional growth (white regions), by Terry Holesinger, LANL.

F. Sm123 Efforts:

An important finding of the research up to this point is that very rapid growth of YBCO is established and is due to both the liquid assistance and to the freedom from having to remove the fluorine that restrict other processes. Attempts to extend this process to SmBaCuO were made. Sm in place of Yttrium is attractive from the evaporative process because of its order of magnitude higher vapor pressure, which permits the use of induction heating in place of electron beam heating. This could be used for all the Sm, Ba and Cu sources and simplifies the rate control, both with lower costs in capital equipment and operation.

The effort did show the feasibility of Sm123 in this precursor process, however the reduction in funding at this time did not allow this approach to be fully explored. Sm123 is different in its growth kinetics and stability from YBCO and will require somewhat different procedures. Additional effort will be required

20

before we can be sure that this process for YBCO can be applied to Sm123. The limited effort is summarized briefly next.

Exploration of SmBaCuO using the Stanford liquid assisted growth of precursors:

Using the knowledge and methods summarized above used on YBCO, efforts were started on SmBaCuO.

Initial efforts were to determine the Stability Diagram for Sm123 relative to YBCO. This was done using two methods:

1. PLD in situ deposited at selected oxygen and temperature.
2. PLD precursors placed the XRD dome and scanned over the temperature and oxygen pressure.
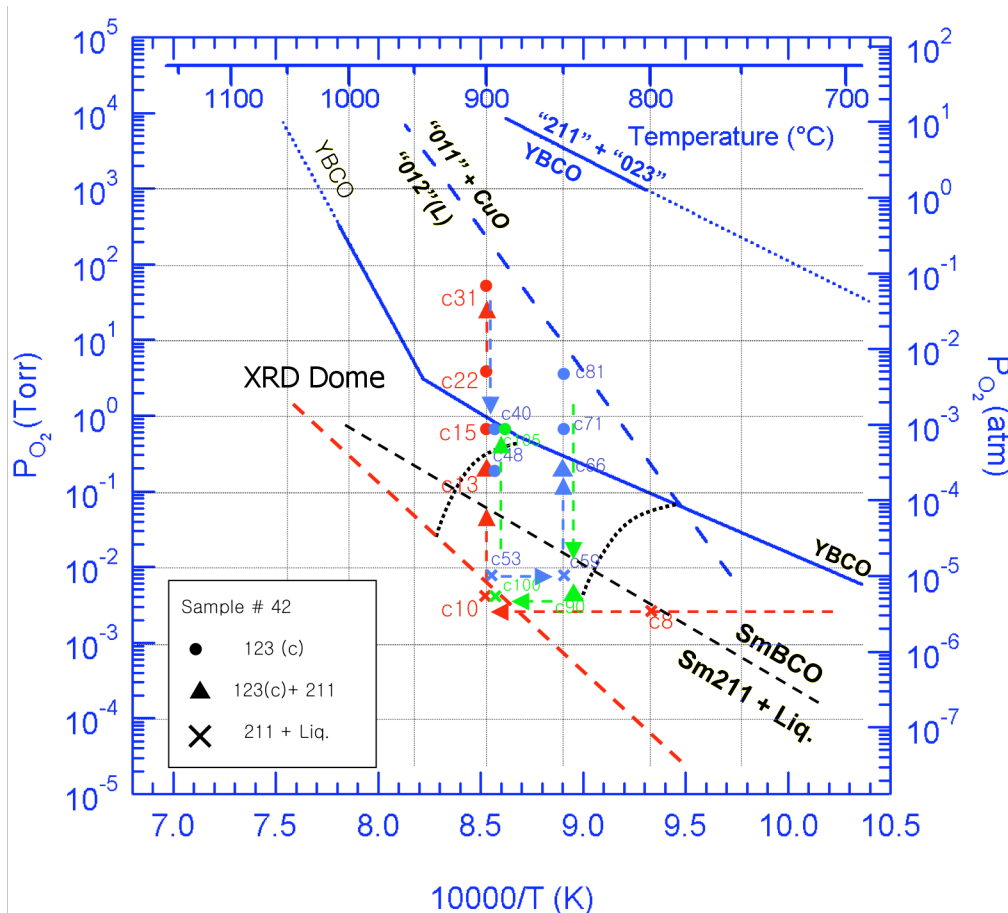

Fig 13: Stability diagram of Sm 123 determined by XRD dome using precursors in black dashed line. XRD scan number with arrows show path taken. For comparison the stability limits found by in-situ PLD are shown in red.

Fig 13 shows the result of determining the stability limits by two methods:

- XRD Dome scanning at each oxygen pressure and temperature shown, using a PLD precursor.
- PLD in-situ deposition at selected points, and later XRD determination of structure.

Conclusion:

- Stability is like that of YBCO, but extends to lower oxygen and higher temperatures.
- Growth from the precursors is different: most paths do not result in "c" only, but also "a" axis partially or mostly, and 211 and 011 phases--see cubic at very low temperature. However a unique method was developed that does result in good Sm123 growth. See the comment below.
- Reaction sluggish ---- 10-20 minutes at 900 C, 1 Torr oxygen to start growth
- Suggests Sm goes to Ba sites, or anti-site-disorder.
- 012 liquid has the same importance as in YBCO.

Overall conclusion of precursor processing:

- Sm 123 is not like YBCO. It is very difficult to grow good "c" axis free from "a" axis and other phases using the growth from the precursors. However, if the process can be restricted to being placed into the stable region suddenly, such as delaying the nucleation as discussed next, or if the transisition can be made very fast—rapid oxidation reaction---this process is possible.

- However good quality pure "c" axis Sm123 using precursor was found if the nucleation from the glassy amorphous state was delayed until the stable region was reached. This was shown by a sandwich of a thin YBCO precursor followed by a thicker Sm123 precursor such that when oxygenated at 830 C the YBCO nucleated at its stability boundary and this induced the Sm123 to nucleate and grow as a pure "c" axis film.

During the above effort on the Sm123 a new effect was accidently discovered.

Key Discovery: Composition Clusters:

In-situ PLD growth of Sm123 Explored:

In the process of exploring the stability region of Sm123 it was accidently found that in a narrow window of oxygen pressure and temperature during the in-situ growth of SmBaCuO an anomalous result was discovered. The XRD showed a

very clean "c" axis, i.e., no "a" or other phases, but had two "c" lattices. Off axis diffraction revealed:

- A nominal orthorhombic lattice with a nominal "a", "b", and "c" lattice,
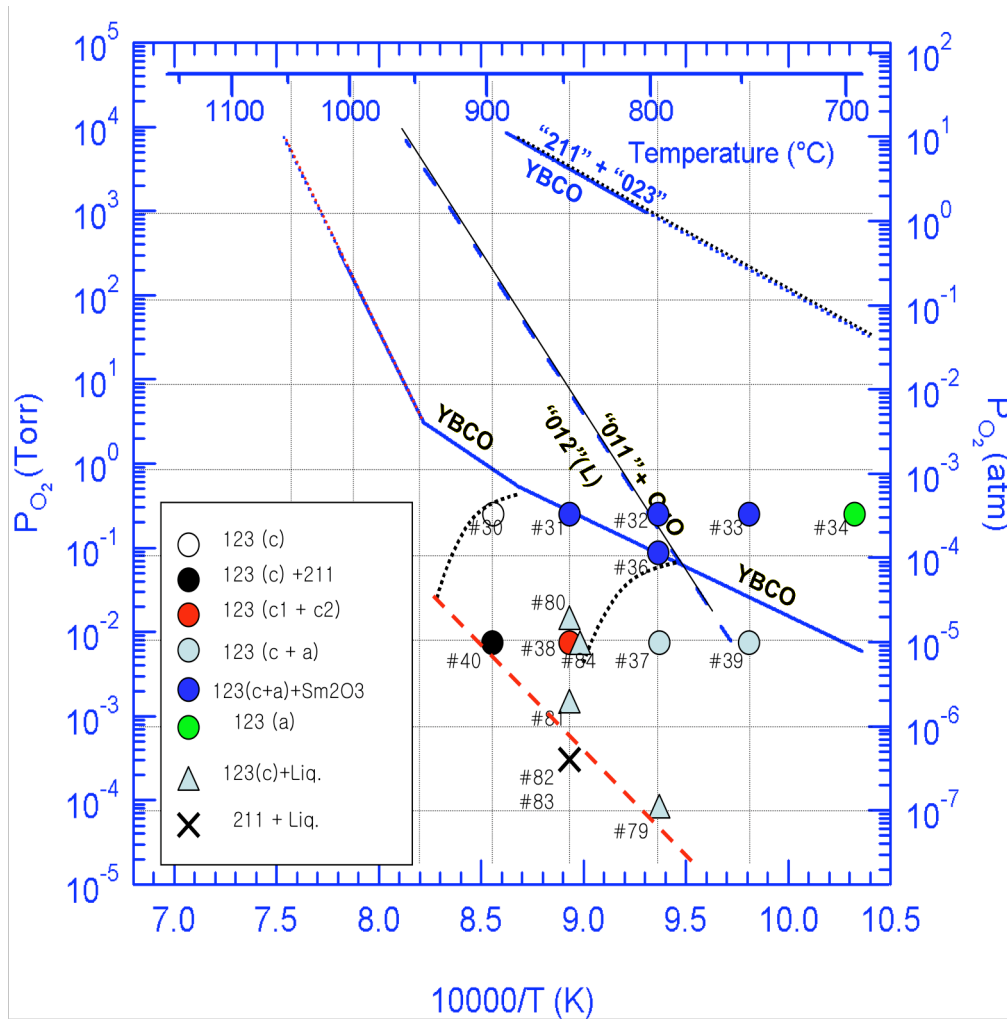- An anomalous tetragonal lattice with a 1 % larger lattice constant.

Fig 14. Stability Diagram of PLD in-situ Growth of SmBaCuO

Fig.14 shows the YBCO stability region (solid lines), and the stability of SmBCO as found in the in-situ PLD investigation (red lines). Note that this line is probably influenced to lower pressure by the activated oxygen in the PLD plume.

An <u>anomalous result</u> was discovered for samples made in the region on Fig. 14 at 10^{-2} Torr (10 mil Torr.) and 850 C (indicated). The XRD showed a very clean "c" axis, i.e., no "a" or other phases, but had two "c" lattices. See fig 15. Investigation of the off axis diffraction revealed:

- A nominal orthorhombic lattice with nominal "a", "b", and "c" lattice constants.
- An anomalous tetragonal lattice with a 1 % larger value.

Figure 16 shows the details of the off-axis analysis. Peak fitting is consistent with an orthorhombic phase and a tetragonal phase.
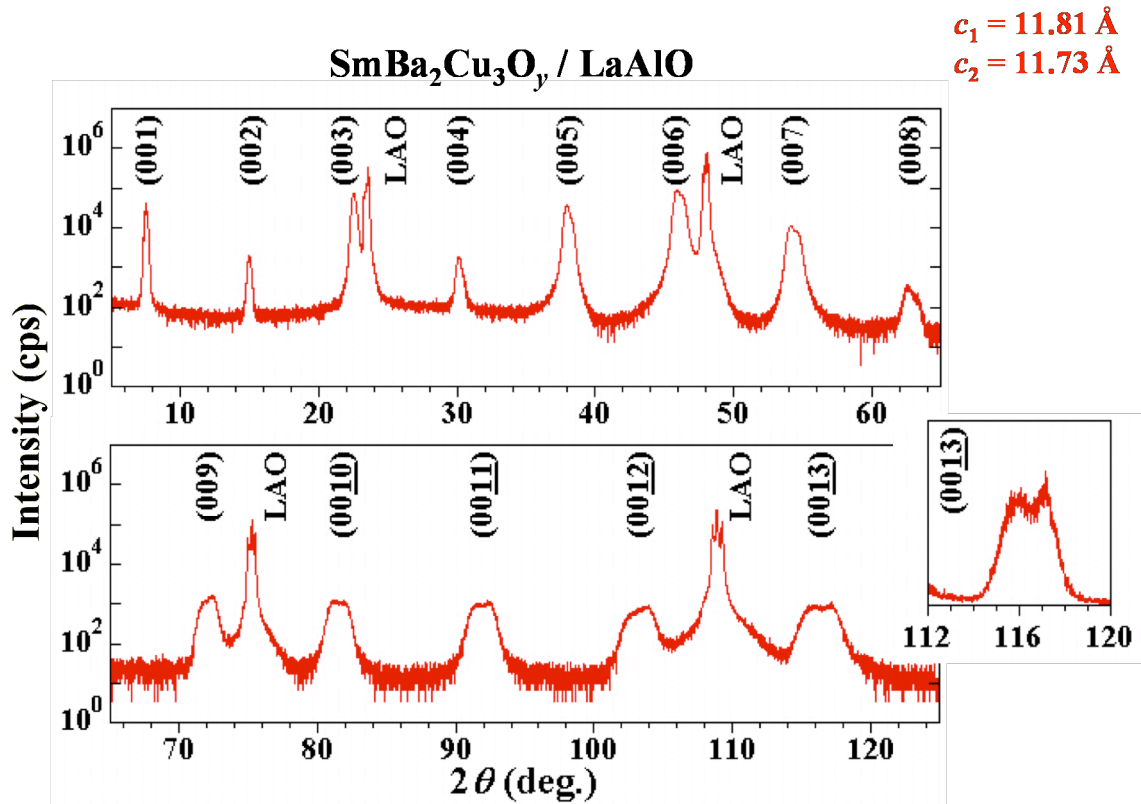
$c_1 = 11.81$ Å
$c_2 = 11.73$ Å

SmBa$_2$Cu$_3$O$_y$ / LaAlO

Fig 15. XRD scan of sample # 38. Only pure "c" axis peaks were found. The insert is a linear scan plot of the 0013 line, showing the two lattices with the measured values shown.
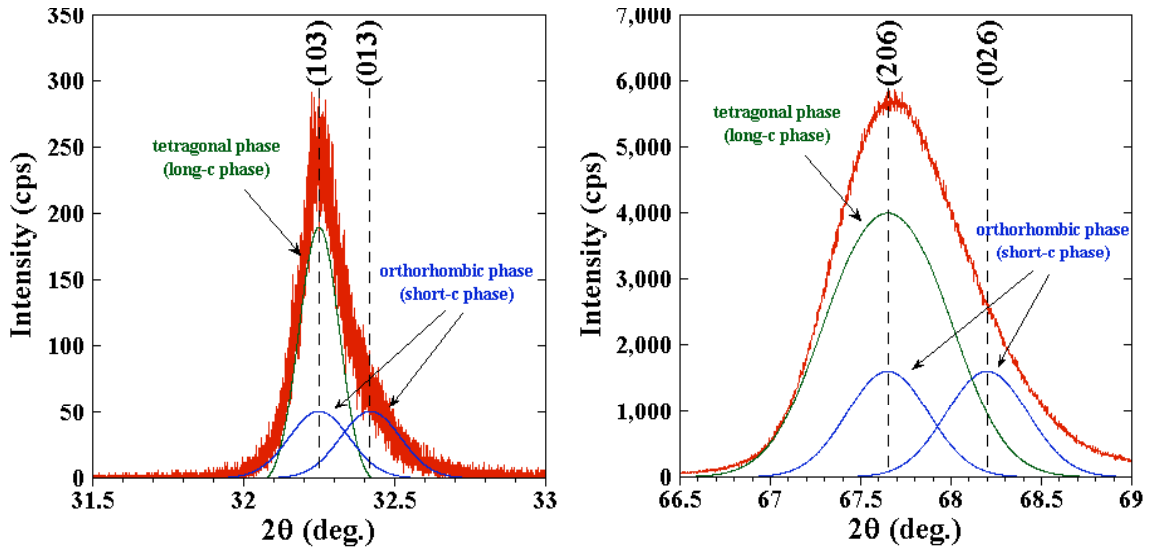
24

Fig 16. Off axis analysis of # 38 showing curve fitting that results in a orthorhombic and a tetragonal lattice.

A reciprocal lattice map (RLM), Fig 17, confirmed that there are two lattices in the growth. Apparently the orthorhombic phase, shown here as the higher 2-theta near to the sharp peak (the 002 LAO), has a larger volume than the tetragonal phase, when integrated over all angles. This is important in explaining the normal state resistivity (Fig. 20 below). In order for the resistivity to have the shape it has the conducting path through the sample must be nearly perfect characteristic of the HTSC, i.e., linear with extrapolation to zero, and a room temperature resistivity about .250 to .300 m ohm-cm. If we assume that the tetragonal phase is non-conductive it must be the minor phase in order for the room temperature resistivity to be about 50 % higher than ideal. If the tetragonal phase is conductive the orthorhombic phase would have a larger normal resistance.
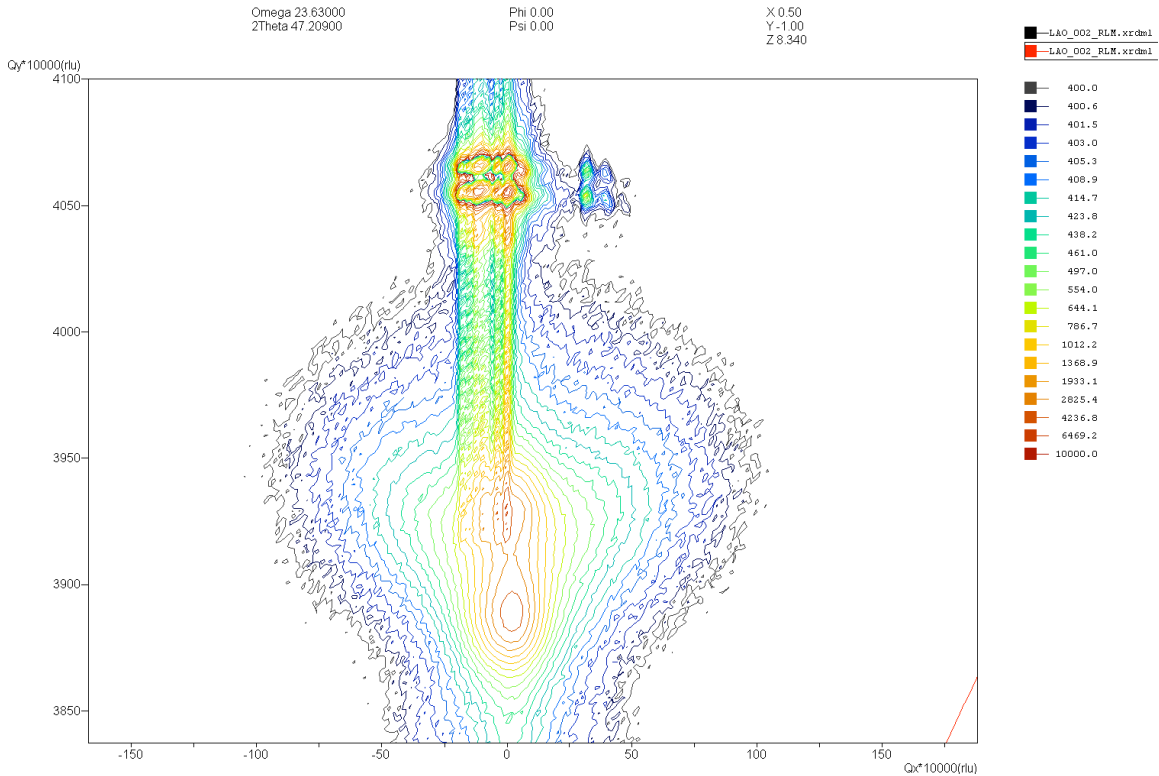
Fig 17. Reciprocal Lattice Map of sample # 38 at the 006 line, and the 200 LAO substrate. The lower peak is the large lattice tetragonal.

The fact of two separate lattices can only be explained if the growth resulted in a clustering in two kinds of Sm 123. Samples made at 100 nm and 1000 nm were compared in XRD with the sample above made at 500 nm thickness. These showed the same result, which means that the growth is not segregated in thickness, but is uniform in the growth direction. The sample at 1000 nm (sample # 182) showed a room temperature resistivity that is about 8 times expected. The reciprocal lattice mapping of # 182 (Fig 19) shows that the tetragonal phase is larger, thus confirming in general the resistivity observed. The reciprocal lattice map for # 38 (Fig 18) at the 0012 line (to compare with # 182 below) shows the reverse is the case here---the ortho is larger ---this is consistent with the almost nominal resistivity. The sample with a thickness of 100 nm is similar in resistivity. At this time we do not have good control of the temperature and oxygen to make reproducible samples. This is addressed later.
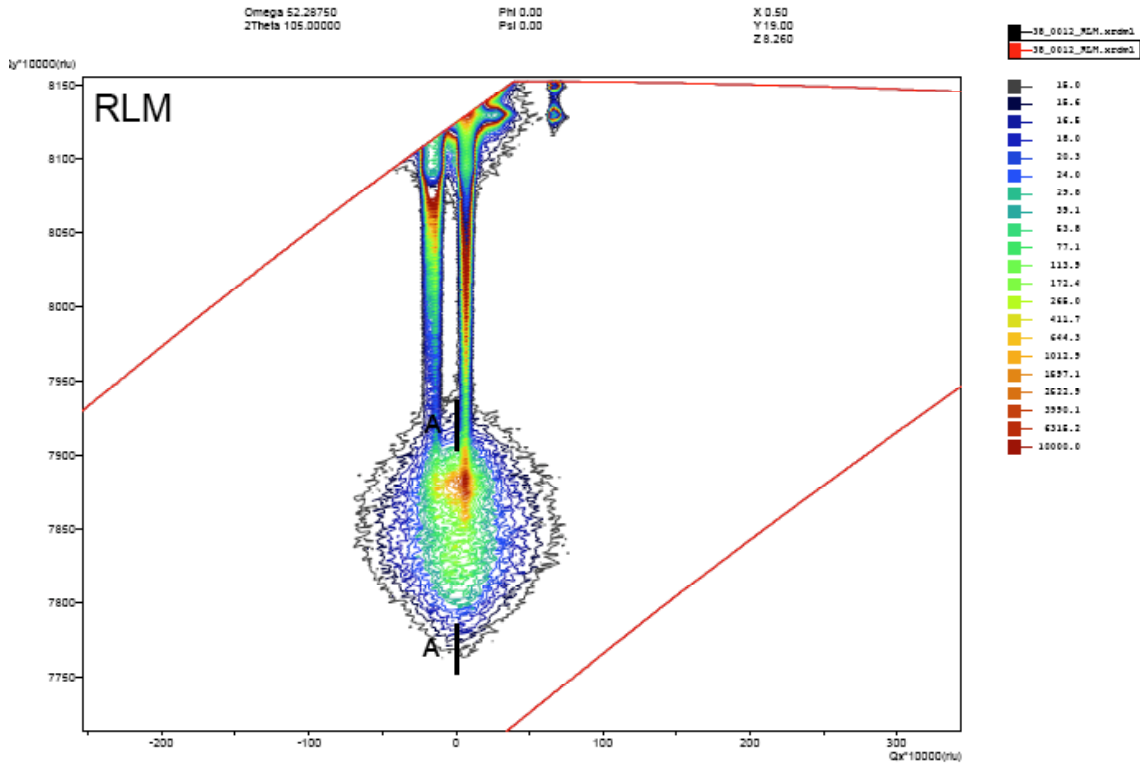
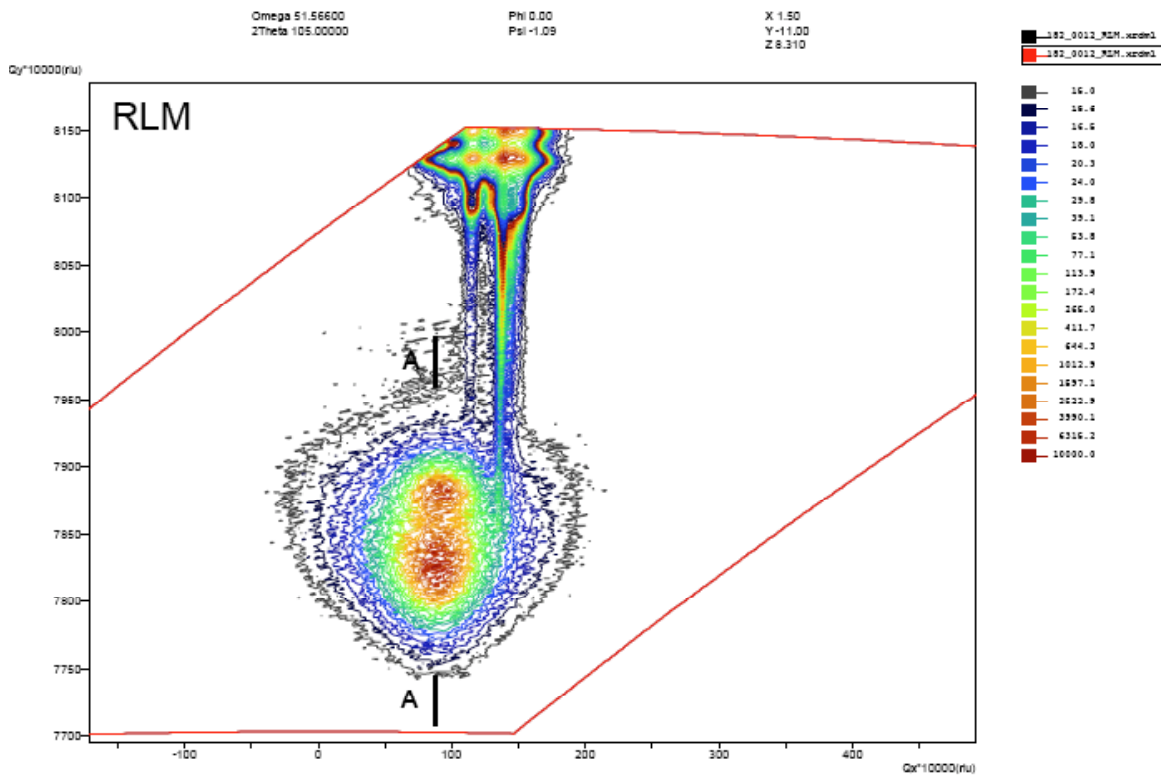Figure 18. RLM of sample # 38 at the 0012 line.

Figure 19. RLM of sample # 182 at the 0012 line. Note that the lower peak is the tetragonal and is larger than the orthro.

It probably will require some TEM effort to reveal the structure, but we suppose that there is a driving force during the deposition and growth that causes lateral segregation into clusters. Another clue is the resistivity vs. temperature, Fig. 20. It is very nearly the perfect curve expected for high quality Sm123. One explanation is that there is a matrix of the nominal orthorhombic structure carrying the current, and a non-conductive structure which is tetragonal within the matrix. The larger lattice constant can be explained by Ba atoms on the Sm site. Sm atoms on the Ba sites has been shown to decrease the lattice constant. That this structure is found at the low oxygen could be explained by a model where the segregation is driven by the low oxygen, and resulting oxygen vacancies. To balance the +2 Ba on the +3 Sm site may require a -2 oxygen leaving the CuO_2 plane (the closest oxygen site). However this results in too large a charge change. By sharing the extra negative missing charge neighboring unit cells would be attracted to each other. This can lead to a model similar to that used to explain the clustering in the case of excess Sm (at higher oxygen pressure than considered here), as in Sm123ss. Sm123ss results when additional Sm is added (which is not the case here). Sm 1+x Ba 2-x Cu 3 O y is a solid solution. Under certain conditions of oxygen and temperature there is clustering which was the motivation of this work, and has been used to explain the so-called peak effect in bulk Sm123ss, and the thin film high field pinning by Yoshida and Matsumoto. In this case the driving force for clustering is high oxygen pressure resulting in oxygen atoms on the 'anti-chain" sites, needed to (or allowing the) balance the additional change in charge from Sm^{+3} on Ba $^{+2}$ sites.

To distinguish our proposed clustering from that which we think explains the peak effect and the Yoshida results, we call our results "**anti-site disorder clustering**".

Note that we see no evidence of excess Sm (nor Ba) in our XRD results. This is not conclusive, as the excess Sm displaced by the Ba on the Sm sites may not be XRD visible at our sensitivity.
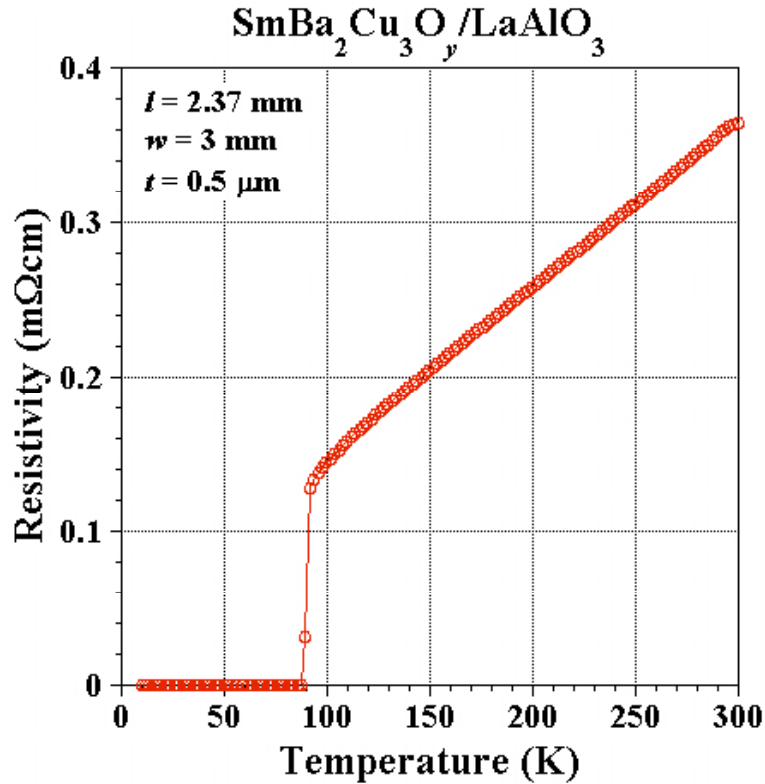
Fig 20. Resistivity vs. temperature of sample # 38.

Note that in both cases the driving force for clustering is low oxygen during growth. The "anti-site disorder clustering" is found at lower oxygen than found for the "composition clustering".

In order to explore the results in the discussion above, we have made a new series of samples to further explore the occurrence of the two phases, the nominal orthorhombic and the new tetragonal clustering. The samples explored a range of substrate temperature and pressure of oxygen, in order to:

1. Verify the repeatability and robustness of the above, and
2. Find the range in T and PO2.

A series of 7 runs were made with 3 substrates per run. The runs covered the range of temperature (indicated only—the actual is probably 50 to 60 C lower based on optical pyrometer and other experiments) from 800 C to 875 C, and

insitu pressures from 50 mTorr down to 10 mTorr (the limit now). No attempt at post anneal was made so far.

The results show that the 2-cluster growth is present from 800 C to 850 C in the pressure range 10 mTorr to 20 mTorr.

The temperature of 875 C at 10 mTorr (# 167) is too high, resulting in 123 + 211, similar to # 40 made at 900 C/10 mTorr. The structure for both appears to be tetragonal. 50 mTorr is too high in oxygen, showing some "a" axis. Thus the window appears to be limited to from 800 to 850 C in temperature and 10 to 20 mTorr in oxygen (10 mTorr is the limit available now---going to lower oxygen would be interesting). This conclusion needs to be examined with further study of the effect of annealing in oxygen. Previously changes were seen after a 300 C in one atm. oxygen for one hour.

In addition runs were made using a target with excess Sm: Sm1.2Ba1.8Cu3 Oy. These samples await annealing, but the tentative conclusion is that the added Sm suppressed the substitution of Ba on the Sm site. Samples made at 825 C/10 mTorr. with and without additional Sm show that the Sm addition prevented the Ba from going into the Sm site, and kept the structure ortho, but disordered ($\Delta(2\Theta)$ large, and R(T) resistivity large). This may be due to some Ba interchange. The details of the Ba-on-Sm sites results above leave uncertain if the Sm also sit on the Ba sites. A future experiment could use a target rich in Ba to suppress this possibility to see if the results of lattice constant are different. The driving force for Sm-on-Ba sites is high oxygen pressure, the opposite of the case here, of Ba-on-Sm sites.

The main questions above are answered:

1. The 2-cluster result are repeatable,
2. There is a small window in T and P.

However there are many questions remaining, the main ones being:

1. What is the driving force for the clustering?
2. Are the size and positions of the clusters good for pinning at high fields?

To answer the latter question samples are needed with R(T) appropriate to good Jc measurements. In order to routinely generate such samples it will be good to (if not needed) to understand the conditions for the clustering.

The next step is to answer some of the questions regarding these:

1. a). Is the clustering only effective during the deposition/growth at the T and PO2 ? What is the effect of post-annealing? Is it effecting only the oxygen positions and amount, or are the anions also moved around, even at say 350 C? Can we learn by annealing at different regions of T, P? If low pO2 is the basic driving force for clustering, should explore low oxygen at various T, consistent with remaining in the stability region.

b). Is there an effect of the time delay between PLD pulses? Would changing the delay by changing the frequency change the clustering? What will be the effect to using continuous co-deposition at various rates? Will the size and separation of the clusters be a function of the diffusion time, and thus the PLD rate and the rates in general? Behind these questions is the notion that the driving force to clustering at the low oxygen used is due to lowering the Gibbs energy by enabling the sharing of oxygen charge between unit cells. To allow the clustering it seems that atoms must be free to move rapidly. Thus this picture involves the surface and the mobility it permits. Thus once within the bulk the mobility is lost and the effect is lost.

2. What is the physical reason for the tetragonal lattice? We assume it is the disorder between the Ba and Sm sites. We have samples that are purely tetragonal, and these are being examined using detailed XRD and perhaps EXAFS. Is it reasonable that these have Tc's of ~ 72 K and 35 K? The tetragonal phase is found at 10 mTorr and temperatures of 750 C (#39) and 875 C (# 166), bracketing the window of the 2-phase region. The # 39 XRD are strong and narrow, and the lattice increased after annealing to a very large value of 11.868, which is not expected nor seen on other samples. The R(T) of this sample is unique in having a liner shape with a single sharp drop at 35 K. It is almost as if a new ordered and stable phase has been formed. The apparent Tc when with the orthorhombic phase is in the range of 72 K, perhaps increased by the proximity effect of the 90 K orthorhombic, or due to different doping (Note that this is saying that the tetragonal phase is a superconductor, or that it contains traces of the orthorhombic phase. This needs to be examined).

We now realize that all of the past runs were made under conditions of T and PO2 that were not reliable and repeatable. In order to make consistent samples and to extend the range of variables the following are necessary:

1. P O2: The present methods of control and measurement are not reliable— need to obtain better control of the pressure of oxygen at 10 mTorr and below. Going to lower than the present 10 mTorr is needed and could lead to interesting important results.
2. Temperature: The present control of the substrate temperature is not reliable. A new substrate furnace has been obtained that will help in this regard.

<u>Summary of SmBaCuO Insitu Results:</u>

- Verified the repeatability and robustness of the cluster in 10 new samples.
- Established the range in T and PO2 in which the clusters are formed, namely in a window 800 C to 850 C, and in the pressure range 10 mTorr (or lower?) to mTorr.

- Determined that the tetragonal phase with the long c-axis is <u>not due</u> to:
  - Oxygen deficient Sm123, supposedly due to the low PO2 growth.
  - Lattice strain due to lattice mismatch between substrates and film. See the article published in the IEEE by A. Tsukada et al referenced later.

- Argued that the tetragonal phase is the result of Ba and Sm inter-site exchange.
- Explored the use of Raman spectroscopy, which may prove to be a tool to characterize the structure on the phases.

Recommended Future Plans (for SmBCO clustering research):

1. Modify the pumping by-pass at the PLD facility to allow lower ranges of PO2 during the in-situ growth. This will permit the investigation of the lower range of the window of the formation of the clusters and with greater precision and repeatability.

2. Install a new substrate heater with improved temperature repeatability and measurement accuracy.

3. Explore annealing of existing samples at different conditions in order to learn the mechanism of the cluster formation and the effect of oxygen doping on the clustering, using XRD and transport measurements.

4. Explore cooling at the growth oxygen pressure to room temperature, followed by characterization, including in the XRD dome at various oxygen pressures and temperatures.

5. Characterize samples with the tetragonal structure to understand the atomic positions in the lattice. Samples are now being examined by Raman Spectroscopy and SEM (Korea), detailed XRD including EXAFS (Stanford), and later by TEM (Korea and Stanford). Samples with both structures will follow.

6. Measure $Jc(H(\Theta), T)$ on samples from the above effort with appropriate $\rho(T)$.

G. <u>**Publications:**</u>

L. S. J. Peng, W. Z. Wang, W. Jo, T. Ohnishi, A. F. Marshall, R. H. Hammond, M. R. Beasley, E. J. Peterson, and R. E. Ericson, IEEE Transactions on Applied Superconductivity **11,** 3375-3378 (2001).

W. Jo, L. S. J. Peng, W. Wang, T. Ohnishi, A. F. Marshall, R. H. Hammond, M. R. Beasley, and E. J. Peterson, Journal of Crystal Growth **225,** 183-189 (2001).

T. Ohnishi, J. Uk-Huh, R. H. Hammond, and W. Jo, Journal of Materials Research **19,** 977-981 (2004).

Jeong-Uk Huh, Thesis, Stanford University, 2006.

Gertjan Koster, Jeong-Uk Huh, R.H. Hammond, and M.R. Beasley, Applied Physics Letters 90, 261917 (2007).

Akio Tsukada, In-Gann Chen, Robert Hammond, and Malcolm Beasley, IEEE Transactions on Applied Superconductivity , submitted 19 November, 2008, in press.

H. Accomplishments:

1. Application and refinement of Atomic Absorption using Tunable Diode Lasers, used in this project for rate control of Ba and Y. These will be essential for large scale up of processes using physical vapor deposition. Funded under DARPA grant.

2. Explored use of and meaning of phase stability (in terms of temperature and oxygen pressure) and the use of liquid $BaCu_2O_2$ in equilibrium with Y and RE BaCuO to show a high rate growth process. Initial efforts using atomic oxygen were not completed due to unavailability of oxygen monitor. Patent filed on 10/26/06 covering this process. Results of appeal pending.

3. Discovered very rapid growth of Y and RE BCO using glassy amorphous precursors, leading to:

    - New materials science.

    - A high rate flexible new process with a low Cost / Performance ratio.

    - J_c values of 5 MA/cm^2 on crystal substrates, and 1.1 MA/cm^2 independent of thickness from 0.4 micron to 1.1 micron on RABiTS tape.

4. Application of FTIR (Fourier Transform Infrared Reflectivity) in understanding the synthesis of thin films in situ growth revealing the changes in absorption and reflection (over a range of wave lengths) due to the optical dielectric properties. Technique should be generally useful to other systems. Purchased under a DURIP-AFOSR grant.

5. Discovered anomalous clustering for SmBaCuO grown insitu at low oxygen pressure:

    - Physics of the driving force for clustering is not understood yet, but is suspected that the inter-site exchange of Sm and Ba along with oxygen vacancies with sharing of unit-cells results in lowering of energy.

    - Clusters are potential high field, high current pinning centers.