DOE/PC/95231-25
DIST. CATEGORY UC-112
UTSI-99-05

TECHNICAL PROGRESS REPORT
FOR
UTSI/CFFF MHD PROGRAM COMPLETION
AND RELATED ACTIVITY

For The Period
April 1, 1999-June 30, 1999

July 1999

Work Performed Under Contract No. DE-AC22-95PC95231

Prepared for:
The United States Department of Energy

Prepared by:
The University of Tennessee
Space Institute
Energy Conversion Research and Development Programs

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EXECUTIVE SUMMARY

Maintenance work on the DOE CFFF facility and other related government property remained in suspension in accordance with the stop work order issued by DOE. Environmental remediation and preservation of the facility continued. Final actions were completed to dispose of the soil that was contaminated by diesel oil. Actions are underway to dispose of other wastes.

Progress is reported on the five (5) high temperature superconductivity projects under Task 6. Results are reported for various techniques for annealing cold rolled nickel tapes and applying buffer layer by the Sol-Gel process. Included in the annealing/coating work is one case that involved oxidizing the nickel to nickel oxide which is textured before application of the buffer layer. Work under the Optimum Coated Conductor included a issuing a topical report describing the work on grain boundary grooving in nickel substrates as a function of annealing temperature and time. Also, the work to evaluate the mutual effects of adjacent superconductors. In the cost/performance analysis project, completion of a study on the economics of production of coated conductors by the MOCVD process is reported. In the diagnostics for real time process control project, a topical report that outlines the requirements for control of promising manufacturing processes was submitted, additional work is reported on using absorption spectroscopy as the basis for control of the stoichiometry for the MOCVD process and the work on scatterometry for measuring uniformity of surfaces is summarized.

TASK 1 - FACILITY MAINTENANCE AND PROPERTY MANAGEMENT

- In September 1998, a stop-work order was issued for work activity in the DOE Facility maintenance area. Work to administer government-owned property continued.

- Mr. Richard Price, FETC Property Administrator for this contract conducted a government property audit during June 21-25, 1999.

TASK 2 – REPORTING AND ARCHIVING

April, May and June Monthly Statue Reports were submitted.

The draft Topical Report entitled, "Bench Scale Evaluation of Solution-Growth Based Techniques for Manufacturing HTS Wire/Tape" DOE/PC/95231-18, was sent out on April 5, 1999.

The draft Topical Report entitled, "Characterization of High Temperature Superconductor Film Layers Using Raman Spectroscopy", DOE/PC/95231-21, was sent out on April 9, 1999.

The draft Topical Report entitled, "Life Cycle Cost Study for Coated Conductor Manufacture by Electron Beam and Pulsed Laser Deposition Systems", DOE/PC/95231-16, has been approved by DOE/FETC and distributed April 21, 1999.

The Quarterly Key Staffing Report for period January-March 1999 was sent out on April 16, 1999.

The Subcontracting Report for individual Contractors (SF294) for the period October 1, 1998 through March 1999 was sent out on April 20, 1999.

Received notification from DOE/FETC that the Quarterly Technical Progress Report for the period October-December 1998 was approved.

Approval notification received April 12 on draft Topical Report entitled, "Evaluation of Methods for Application of Epitaxial Buffer and Superconductor Layers", DOE/PC/95231-11.

The Off-Site Contractor's Property Management System Self-Evaluation was completed and sent out on April 22, 1999. The Quarterly Technical Progress Report for the period January-March 1999 was sent out on April 30, 1999.

The draft Topical Report entitled, "An Evaluation of Absorption Spectroscopy to Monitor $Yba_2Cu_3O_{7-x}$ Precursors for Metal Organization Chemical Vapor Deposition Processing, DOE/PC/95231-23, was approved by DOE with minor changes and distributed.

The April Monthly Report was sent to DOE on May 20, 1999.

The draft Management Plan covering the period October 1, 1998 through September 30, 1999 has been approved by DOE.

TASK 3 - SITE ENVIRONMENTAL COMPLIANCE AND REMEDIATION

The diesel-contaminated soil was approved for landfill disposal by the State of Tennessee. In order to receive State approval a $250 per waste stream fee must be sent with application and waste description (2 forms) to the Nashville Office. In addition, a separate set of forms must be sent to the field office. A separate set of landfill company (BFI) forms is sent to the landfill. In summary, a number of criteria had to met before actual hauling and disposal. The actual disposal is scheduled for early July, 1999. Under state guidelines, lead and benzene must be under 5 mg/l by TCLP analysis. The laboratory analysis results were 0.014 and 0.05 mg/l for lead and benzene, respectively, well under the 5 mg/l limit. The soil will be hauled to the BFI Middle Point landfill in Murfreesboro, TN.

A property audit was conducted by DOE/FETC representative Rick Price during the month of June 1999. Several items concerning salvage and waste were discussed. Of particular interest were the 19 remaining TRW tote bins, partially filled with spent seed and ash. Mr. Price stated he would expedite the release of this property in order that UTSI could dispose of these.

Non-hazardous wastes - but probably "special waste" rating - are being managed until disposition can be resolved. These wastes include, but are not limited to, raw coal, drums of coal and ash, sludge, facility water and salvage metal.

The CFFF holding pond water discharge was monitored and monthly reporting was accomplished with no out of permit limits noted.

The analysis of the last well was completed and lab report received. This well was sampled for VOCs, and no chemicals were "seen" that were above drinking water standards for the constituents of concern requested by the State. Plans are to complete additional sampling in the month of August and November of 1999.

TASK 4 - SITE REACTIVATION

No work was scheduled or performed.

TASK 5 - DISASSEMBLY AND DISMANTLEMENT (D&D) OF THE CFFF

No work was scheduled or performed.

TASK 6 - ADVANCED TECHNOLOGY, RESEARCH, DEVELOPMENT AND ENGINEERING FOR OTHER FEDERAL OR DOE PROGRAMS

Subtask 6.02 Evaluation of Methods for Application of Epitaxial Buffer and Superconductor Layers

A technical paper entitled, “Review and Evaluation of Methods for Application of Epitaxial Buffer and Superconductor Layers” was proof-read and scheduled to be published in the Journal of Applied Superconductivity, published by Elsevier Science. So far, twenty-one scientists from all over the world have requested a copy of the preprint and each of these requests have been satisfied. Similarly, several requests for our other paper entitled, “Bench Scale Evaluation of Batch Mode Dip-Coating of Sol-Gel $LaAlO_3$ Buffer Material” to be published in IEEE Transactions on Applied Superconductivity have been satisfied also. United States Department of Energy contract officers (Dr. Udaya Rao and Mr. Roland George) have been provided lists containing names and addresses of these requests.

$LaAlO_3$ Application on Cube Textured Nickel

A new thermal processing chamber and a new insertion/removal mechanism were completed during May and functioned well. The chamber consists of an approximately 2.5 inch OD and 4 foot long quartz tube with one end closed and the other end having an o-ring sealed cap with gas and thermocouple feedthroughs. The quartz tube is held by a fixture attached to a linear slide, which enables the tube to be easily inserted into or withdrawn from the furnace without manual handling and the attendant risk of breakage. $LaAlO_3$ coated samples are held in a quartz crucible attached at the end of the thermocouple.

Half-inch wide by about five-inch long tapes of nickel provided by Plastronic, Incorporated were annealed at the University of Tennessee Space Institute by resistively self-heating at very near the melting point in a high purity argon atmosphere for times ranging from 5 minutes to 20 hours. Annealing produced cube texture nickel samples whose sharpness increased with annealing time. For example, the 20-hour annealed nickel had a Ni (200) RD omega Gaussian FWHM of 7.0 degrees, Ni (111) phi Gaussian FWHM of 6.8 degrees, and 0.1 volume percent twinning while the one-hour annealed nickel had a Ni (200) RD omega Gaussian FWHM of 8.7, Ni (111) phi Gaussian FWHM of 7.9, and 0.4 volume percent twinning. Perhaps a more consequential effect of annealing time on the ability to deposit well textured buffer layers than texture sharpness is believed to be the depth of resulting grain boundary grooving and surface roughness within the grains.

Lanthanum aluminate films were first coated onto annealed nickel strips that possessed deep grain boundary grooving. These nickel strips had been annealed for twenty plus hours at 62-63 amps. The surface roughness on these samples was considerably high. The first several coated samples produced had the following properties. The in-plane texture of the samples varied from 19-26 degrees [Phi (111) FWHM] and about 25% of the $LaAlO_3$ grains were rotated 45° in-plane. Out-of-plane texture ranged from 12-15 degrees [RD Omega (200) FWHM]. Phase scans likewise showed the absence of good (100) out-of-plane texture. It was thought that these rather poor results may have been due, at least in part, to the surface roughness.

One attempt to diminish any effects of surface roughness was to electropolish and then ultrasonically clean samples as part of a new preparation scheme. A 70% acetic acid/30% perchloric acid electrolyte mixture was used with a Buecher Electromet III metallographic electropolishing apparatus. Samples were electropolished from one-half minute to one minute at 25 volts. The average phi and omega scan results were respectively 10.8 and 10.7 degrees FWHM. The amount of 45° in-plane rotation in the samples rose to about 30% on the average, and the out-of-plane texture of the samples improved only slightly. The phase scans showed that the (110) peak still had an amplitude on the average of 77% of the (100), while (111) peaks were in the order of 15% of the (100). Due to some limitations of the electropolishing apparatus (poor mixing across the sample face leading to burns or areas of unevenly high current density), Able Electropolishing of Chicago, Illinois was given an annealed strip of nickel to do a trial polish with their commercial process.

In the meantime, another alternative to electropolishing was explored. This involved only annealing the samples for short amounts of time (less than an hour) to reduce the grain boundary grooving. On average the omega and phi scans were 14.6 and 17.0 degrees FWHM, respectively. In-plane 45° grain rotation rose slightly to 33.5% and the out-of-plane texture remained virtually the same. As a result of worsening results, a modification was made to the thermal processing temperature profile. A half-hour to one hour holding step at around 550°C was added in hopes of increasing the degree of sintering, in case the pores in the gel were not being filled or perhaps additional pores were forming from the release of chemical water (terminal organic groups leaving to form alcohol). However, phi and omega scan FWHMs increased to 17.8 and 23.2 degrees, respectively. In-plane rotation remained the same at 32%.

Some scatter in the results for these small size samples may have resulted from substrate edge effects on film growth. To evaluate these effects, a strip around 5-6 inches long was coated to about 80% of the length. Two different regions of the coated material were evident on this strip with the naked eye. A long top segment appeared to be thin and uniformly coated, while a bottom segment about one-half inch long at the bottom of the sample had a thicker non-uniform coating. X-ray scans were performed in both the top and the bottom segments. The scan results for the bottom segment were poorer than those for the top. A (111) peak was not evident in the phase scan of the top portion, but was found in the bottom portion (47% of the height of (100), in fact) along with (110) at 77% of (100) as compared to 55% in the top segment. Omega and phi FWHMs were higher in the bottom segment, up from 20.7 to 29.3 degrees and from 14.1 to 19.3, respectively. However, the percent of in-plane 45° rotation remained the same at 28 percent.

Attempts were then made to explore the possibility of using a cube textured nickel oxide on the nickel substrate prior to coating. This initially proved unsuccessful with omega and phi scan FWHMs well into the 20s. A new batch of precursor solution was made at this point, in case the fault was with the solution. Some of the previous problems encountered in making up precursor solutions, including precipitation of brown particles, probably La, due to moisture contamination or sensitivity to high heating ramp rates or pressure buildups, were also corrected with some modifications to the distillation apparatus. Modifications included a vacuum pump and a valve to release to atmosphere pressure built up in the still from the vaporizing solvent. Also, all-new batches of ingredients were ordered and used to reduce the likelihood of moisture contamination.

The new batch of precursor solution was used in coating the same 20-hour annealed, deep grain boundary grooved nickel strips (without NiO) that were originally used in the first several samples. Phi scan results reduced to 16.23 degrees FWHM, but the out-of-plane texture worsened, in that omega scans showed an average FWHM of 19.3 degrees. In-plane 45° rotation, however, disappeared from the phi scans and pole figures.

In another attempt with textured nickel oxide films and this new batch of precursor solution, some interesting results were produced. Again, none of the samples showed any signs of in-plane rotation. Phi scans averaged 13.5° FWHM, but the omega scans stayed high at an average of 19.3. The phase scan showed some improvement with the (110) peak at 24% of the height of (100) and (111) at 9% (See Figure 6.02-1). Variation of the furnace time from one-half hour to one hour at 1150°C didn't make any readily discernable difference.

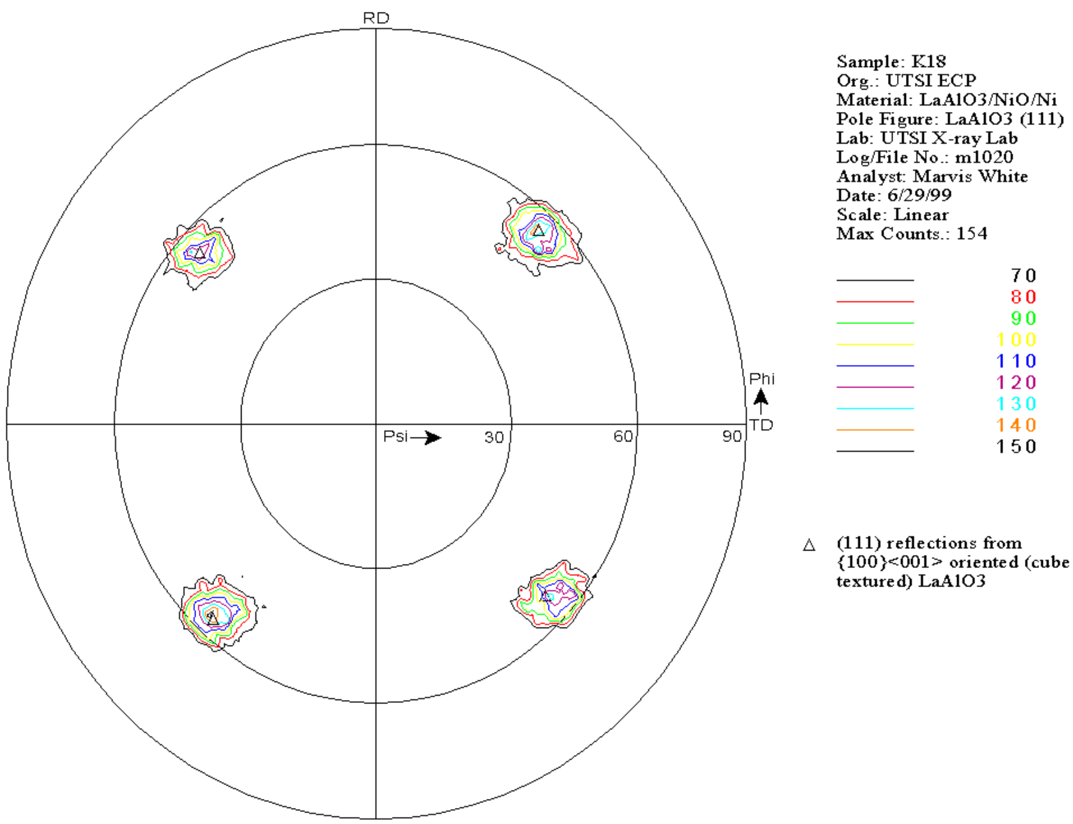


Figure 6.02-1. $LaAlO_3$ (111) Pole Figure of a Typical NiO/Ni Sample with a $LaAlO_3$ Coating on Top. No 45° In-plane Rotated Component Exist

Subtask 6.03 Coated Conductor Development and Program Management

Routine program management continued. Preparations began for the 1999 DOE Peer Review in July. DOE decided that it was not necessary to revise the development roadmap for coated conductors at this time.

Subtask 6.04 Optimum Coated Conductor

A topical report (DOE/PC/95231-27) describing the study of grain boundary grooving on nickel substrates as a function of annealing time and temperature was completed and forwarded to DOE/FETC for review.

Experimental investigation of the critical current under self-field at liquid nitrogen temperatures continued during the quarter. Silver/BSSCO multifilament tape is used as the superconductor for the studies. The studies are conducted with tapes in the length of 30 to 100 centimeters. The initial measurements were made with a one-meter long tape having a cross sectional are of 0.0097 cm^2 and the critical current density was found 494 A/cm^2. Actually, based on the overall one meter length and a one microvolt/cm criteria, the gross critical current density was only 356 A/cm^2, but the tape proved to have a flaw in it such that the voltage drop per unit length was not uniform and most of the observed drop occurred at one location. The higher value of current density corresponds to the same criteria over the apparently unflawed length of the tape.

A continuation experiment using several lengths of tape in parallel was formulated. The idea was to measure the current distribution between tapes as a function of the spacing between the tapes to simulate the geometry of a coated conductor. Implementing the experiment, however, is proving to be a challenge primarily due to the fragility of the superconducting tape. Mechanical connection of the lead wires to the superconducting rape is not possible because of the proximity of the mechanical connectors to each other when the three tapes are laid alongside of each other. Soldering can introduce unknown problems as well. For example, the soldered connections can be checked at room temperature for low resistance, but this only verifies the silver to copper lead-in connection and ignores the encapsulated superconductor integrity. By far the biggest problem is that compared to the copper leads, the superconductor is quite flimsy and it is easy to inadvertently bend or twist it if the lead-in wires are not rigidly supported. In addition, there are four measurement leads for each of the three legs of the assembly that will be manually connected to the single nanovoltmeter to measure the currents and voltages in the three parallel conductors.

Subtask 6.05 Cost Performance Analysis of Potential Manufacturing Processes

The cost/performance study of the use of the Metal Organic Chemical Vapor Deposition (MOCVD) process for the manufacture of coated conductors was completed this quarter and documented in a topical report (DOE/PC/95231-26). This report was sent to DOE for review in early July. The base case costs are \$2.26/m of wire and \$5.66/kA-m for a critical current of 10^6 a/cm^2 or \$56.60 for a critical current density of 10^5 a/cm^2.

Work began on a similar study for manufacture of the coated conductor using the sol-gel process.

Subtask 6.06 Development of Real Time Process Control Using In-Situ Diagnostics

The draft report, Development of In-Situ Control Diagnostics for Application of Epitaxial Layers of Superconductor and Buffer Layers, DOE/PC/95231-24, was submitted to DOE.

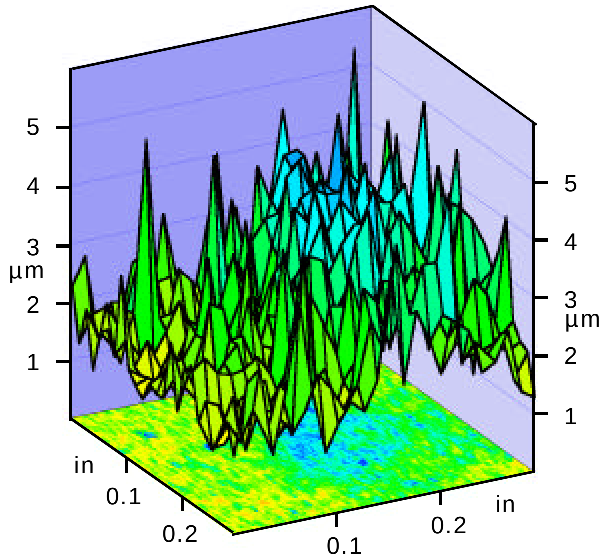
Optical Scatterometry

Work on this topic concentrated on defining the practical application of the technology for the manufacture of coated conductors. The laser used for optical scatterometry can be adjusted to give a small spot size (about 0.1 mm in diameter), which is useful for detailed examination of the surface roughness of a small sample by scanning the surface area being examined through the spot. This technique takes times of the order of minutes which are not compatible with on-line, real time control but will give a detailed surface map of a single sample. Examples of this application are shown in Figure 6.06-1, which are scans of the EURUS Type B nickel strip and annealed by UTSI, showing the surface before and after electropolishing.

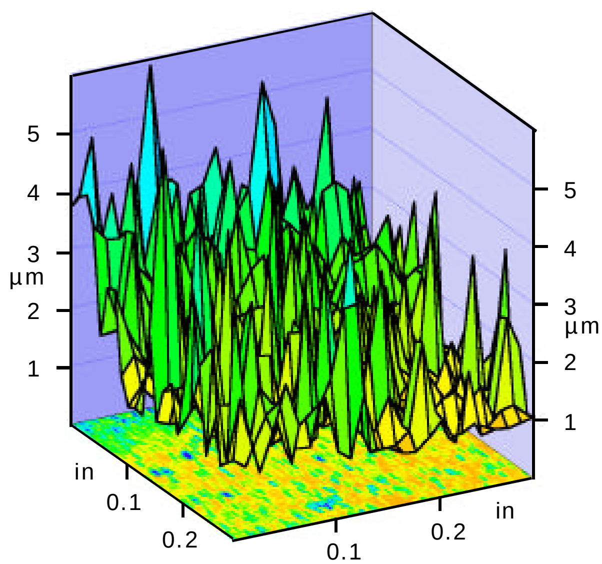
If the laser is adjusted for a larger spot size (7mm long by 1.5 mm wide), the system can be used to scan along the length of the tape to provide an indication of major quality problems in real time. This can be used to at least tell the control system when problems occur. It is estimated that such a system can scan at least 100 cm^2/sec.

Absorption Spectroscopy of MOCVD Precursors

Because ultraviolet (UV) spectral absorbances acquired earlier on copper, yttrium, and barium *THD* MOCVD precursors were more than an order of magnitude less than previously published absorbances[1,2], experiments were initiated simulating the previous studies. These previous studies measured absorbances for the *THD* compounds solved in n-Hexane, so UV spectroscopic grade n-Hexane was acquired. In addition an alternate supply of $Ba(THD)_2$ was obtained because previous results indicated that the old $Ba(THD)_2$ degraded during its year-long storage. (*THD* represents 2,2,6,6-tetramethyl-3,5-heptanedionato, as in $Ba(THD)_2$, and is also referred to as *DPM* for dipivaloylmethane.) These studies were delayed because the n-Hexane and the replacement $Ba(THD)_2$ were repeatedly back-ordered until an alternate source of the $Ba(THD)_2$ was secured. The new $Ba(THD)_2$ arrived at the end of the quarter and was of a slightly different color than the old $Ba(THD)_2$, further indicating degradation of the old $Ba(THD)_2$.



a. Annealed Ni with Anomalous Scatter



b. Electropolishing

Figure 6.06-1 Measured Roughness of Plastronic B Annealed Nickel.

Scans of the UV transmissivity of the optical cells located for the solution experiments showed adequate transmission even at 200 nm for the cells but marginal transmission below 215 nm for the cells filled with n-Hexane. Marginal transmission similar to the n-Hexane transmission was achieved for wavelengths less than 220 nm with the chamber having all sapphire windows. A power supply failure, and subsequent replacement, delayed the baseline cell scans until late in the quarter. The measured absorbances for the cell and the cell with n-Hexane are provided in Figure 6.06-2.

Due to high absorption for sapphire windows at wavelengths shorter than 220 nm, baseline signal levels for the previous scans were small at these shorter wavelengths. Thus, to improve absorbance measurements in the 200-220 nm region, new Suprasil® windows were obtained for the oven. Resulting change in the baseline test apparatus absorbance is also shown in Figure 6.06-2.

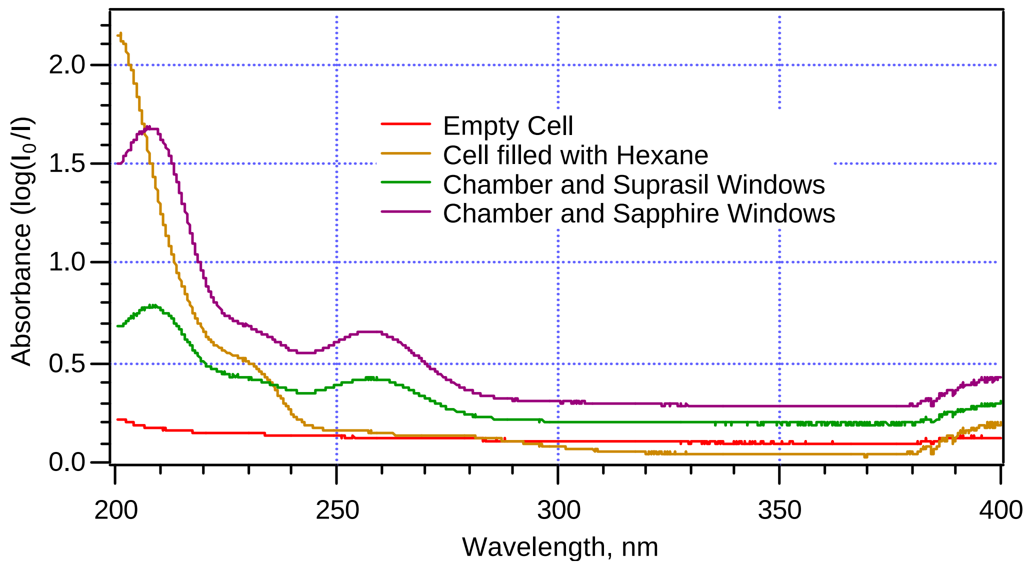


Figure 6.06-2. Quartz Cell and Oven Window Absorbance Spectra, 200-400 nm

Objectives for next Quarter include examination of the combined absorption spectra for *Cu(THD)*$_2$, *Y(THD)*$_3$ and *Ba(THD)*$_2$ to see if their absorption bands are sufficiently distinguishable for simultaneous measurements of precursor species. Verification of the Beer's Law constants for the precursors will be completed at the beginning of the quarter, and the concentration range corresponding to linear Beer's Law response will be identified for each precursor.

REFERENCES

1. Harima, H., Ohnishi, H., Hanaoka, K., Tachibana, K., and Goto, Y., "An IR Study on the Stability of Y(DPM)$_3$, Ba(DPM)$_2$, and Cu(DPM)$_2$ for UV Irradiation," *Japanese Journal of Applied Physics*, 30 (9A) pp. 1946-1955, September 1991.

2. Rappoli, B. J. and DeSisto, W. J., "Gas Phase Ultraviolet Spectroscopy of High-Temperature Superconductor Precursors for Chemical Vapor Deposition Processing," *Applied Physics Letters*, 68 (19) pp. 2726-2728, May 1996.

4. OPEN ITEMS

A. UTSI: None

B. DOE/FETC

Property Retirement Work Orders 15 through 34 are awaiting approval by DOE.

5. SUMMARY STATUS ASSESSMENT AND FORECAST

Maintenance expenditures on the DOE CFFF facility have been stopped. Government Property Administration is continuing on a minimal basis with University funding, but funds are not available for needed maintenance of most government property.

Environmental preservation and restoration activities at the CFFF continue.

High Temperature Superconductor research work is continuing as planned.

Contract reporting requirements are being met substantially on time.

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TASK AND COST VARIANCES

The positive variance in Task 2 is because funds were budgeted in this task in the approved management plan for reporting activities but no funds have been authorized for that purpose by DOE and no charges have been made. The positive variance in Task 3 is because funds were not authorized until later in the fiscal year and activities and expenditures fell behind the management plan schedule. The large negative variance in Task 6 is due to a combination of several factors. A major factor is that the university fiscal year ends June 30th and the June labor, which is normally not posted to the accounting ledgers until the following month was posted at the end of June. Thus, this quarter's actual expenditures show four months of labor rather than the normal three. Additionally, some activities have required more labor than originally estimated. Preparation of several topical reports, in addition to the normal monthly and quarterly reports, have required some labor that was planned for Task 2 rather than Task 6.

APRIL 1, 1999-JUNE 30, 1999 QUARTERLY VARIANCE REPORT

Planned vs. Actual Expenditures

(thousands of dollars)

TASK	PLANNED	ACTUALS	VARIANCE
1	0.0	0.0	0.0
2	10.1	0.0	10.1
3	27.0	20.2	6.8
4	0.0	0.0	0.0
5	0.0	0.0	0.0
6	157.6	329.8	-172.2
TOTALS	194.7	350.0	-155.3

COST ELEMENT			
DIRECT LABOR	97.4	188.1	-90.7
FRINGE BENEFITS	20.5	43.0	-22.5
EQUIPMENT	0.0	0.0	0
EXPENDABLE MATERIAL	8.0	2.4	5.6
OUTSIDE CONTRACTS	4.6	4.3	0.3
TRAVEL	2.4	0.0	2.4
TOTAL DIRECT COSTS	132.9	237.8	-104.9
INDIRECT COSTS	61.8	112.2	-50.4
TOTAL	194.7	350	-155.3

Planned vs. Authorized Funding

Cumulative

Task	PLANNED	AUTHORIZED FUNDING
1	1496.4	
2	604.1	
3	530.6	
4	0.0	
5	0.0	
SUBTOTAL	2631.1	1982.7
6	3518.2	3804.4
TOTAL	6149.3	5787.1