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1. Several wet chemical synthesis routes to the preparation of metal-organic precursors for heavy metal fluoride glasses were developed. Particular attention was directed to the synthesis of double alkoxides and multialkoxides containing various combinations of the desired heavy metal cations.

2. Using selected precursors, it was demonstrated that multicomponent oxide gels could be prepared which contained the heavy metal cations in concentration ratios corresponding to those in the fluoride glass analogues.

3. Conversion of multicomponent oxide gels based on heavy metal cations to the correspondent fluorides was demonstrated.

4. Improved passivation of the surfaces through reaction with sulfuric acid. in a surface layer to the correspond much lower rates of chemical attack attack were measured.

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5. A computer model was developed which described in detail the number and size distributions in an initially liquid body which is cooled to temperatures below the glass transition at an arbitrary rate R_1, reheated at any arbitrary rate R_2 to an arbitrary temperature above the glass transition (as the draw temperature), and recooled at an arbitrary rate R_3 to form the final body. The model provides the capability of predicting material and process parameters which are critical in obtaining good glasses.

6. It was demonstrated that high temperature superconductors in both the Y-Ba-Cu-O and Bi-Ca-Sr-Cu-O systems could be formed by wet chemical routes. The preferred synthesis route involved the use of nitrate solutions. Critical temperatures for superconducting behavior similar to those of the best vapor-deposited films were demonstrated. The approach has significant commercial potential, and a patent disclosure was filed.

7. For a range of compositions in the Bi-Ca-Sr-Cu-O systems, it was demonstrated that glasses could be formed. The ability to form glasses was related to chemistry and knowledge of the kinetic processes involved in glass formation. The crystallization behavior of the glasses was determined, and superconductivity of the resulting crystallized bodies was demonstrated.

8. Using wet chemical synthesis routes based on sol-gel methods, barrier layers having a broad range of chemistries were prepared; and their effectiveness as barriers to interaction between superconducting films and substrates was evaluated. Improvement in critical temperature for superconductivity through the use of such barrier layers was demonstrated.

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AFOSR·TR· 89-1203

TITLE: Synthesis and Crystallization Behavior of Fluoride Glasses

PRINCIPAL INVESTIGATOR: Professor Donald R. Uhlmann
Department of Materials Science and Engineering
University of Arizona
Tucson, Arizona 85721

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SENIOR RESEARCH PERSONNEL: Donald R. Uhlmann

JUNIOR RESEARCH PERSONNEL: M. Aronson, G. Teowee, G. Dale
M. Denesuk, G. Berry, M. Choudry,
T. Gudgel, M. Smith and Kim Hamm

PUBLICATIONS

1. "Superconducting and Structural Properties of Spattered Thin Films of $YBa_2Ca_3O_{7-x}$," J.L. Makous, L. Maritato, C.M. Falco, J.P. Cronin, G.P. Rajendran, E.V. Uhlmann and D.R. Uhlmann, App. Phys. Lett. 51 (1987) 2164-2166.

2. "Wet Chemical Processing of High T_c Superconducting Films," B. Dutta, B. Samuels, J.P. Cronin, G. Dale, G. Teowee, G. Rajendran, E.D. Zanotto, E.V. Uhlmann, B.D. Fabes and D.R. Uhlmann, pp. 501-510 in M.F. Yan, Ed., Ceramic Superconductors II (ACS, Westerville, 1988).

3. "Melt Processing of Bi-Ca-Sr-Cu-O Superconductors," E.D. Zanotto, J.P. Cronin, B. Dutta, B. Samuels, S. Subramoney, G.L. Smith, G. Dale, T.J. Gudgel, G. Rajendran, E.V. Uhlmann, M. Denesuk, B.D. Fabes, and D.R. Uhlmann, pp. 406-418 in M.F. Yan, Ed., Ceramic Superconductors II (ACS, Westerville, 1988).

4. "Bi-Ca-Sr-Cu-O Superconductors of (2122) Composition by Melt Processing," T.J. Gudgel, E.D. Zanotto, G.L. Smith, G. Dale, S. Subramoney, E.V. Uhlmann, M. Denesuk, J.P. Cronin, B. Dutta, G. Rajendran, B. Fabes, and D.R. Uhlmann, pp. 419-427 in M.F. Yan, Ed., Ceramic Superconductors II (ACS, Westerville, 1988).

5. "Wet Chemistry-Derived Barrier Layers for Ceramic Superconductor Films," J.P. Cronin, T.J. Gudgel, L. Zanotto, B. Dutta, G.P. Rajendran, G. Dale, E.D. Zanotto, E.V. Uhlmann, G.L. Smith, M. Denesuk, B.D. Fabes and D.R. Uhlmann, pp. 511-523 in M.F. Yan, Ed., Ceramic Superconductors II (ACS, Westerville, 1988).

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The objectives of the program were as follows:

1. Exploration of wet chemical synthesis routes to the preparation of metal-organic precursors for heavy metal fluoride glasses.

2. Exploration of synthesis conditions for converting precursors to multicomponent oxide gels for conversion to heavy metal fluoride glasses.

3. Exploration of chemistries and conditions for converting multicomponent oxide gels to heavy metal fluoride glasses.

4. Exploration of chemical approaches to passivating the surfaces of heavy metal fluoride glasses.

5. Exploration of the possibility of developing a computer model to describe crystallization during a cycle of cooling-reheating-recooling a liquid to form a glass (the cycle used in forming fluoride glass fibers).

6. Exploration of wet chemical synthesis routes to the formation of high temperature oxide superconductors.

7. Exploration of the feasibility of forming glasses of high temperature superconductor compositions, and of the crystallization behavior of such glasses if obtainable.

8. Exploration of wet chemical synthesis routes to the formation of barrier layers for use with high temperature oxide superconductor films on ceramic substrates.

The accomplishments of the program were as follows:

1. Several wet chemical synthesis routes to the preparation of metal-organic precursors for heavy metal fluoride glasses were developed. Particular attention was directed to the synthesis of double alkoxides and multialkoxides containing various combinations of the desired heavy metal cations.

2. Using selected precursors, it was demonstrated that multicomponent oxide gels could be prepared which contained the heavy metal cations in concentration ratios corresponding to those in the fluoride glass analogues.

3. Conversion of multicomponent oxide gels based on heavy metal cations to the corresponding fluorides was demonstrated.

4. Improved passivation of the surfaces of heavy metal fluoride glasses was accomplished through reaction with sulfuric acid. This reaction converted the heavy metal fluorides in a surface layer to the corresponding heavy metal sulfates, which are characterized by much lower rates of chemical attack in aqueous environments. The kinetics of such attack were measured.

5. A computer model was developed which describes in detail the number and size distributions in an initially liquid body which is cooled to temperatures below the glass transition at an arbitrary rate R_1, reheated at an arbitrary rate R_2 to an arbitrary temperature above the glass transition (as the draw temperature), and recooled at an arbitrary rate R_3 to form the final body. The model provides the capability of predicting

material and process parameters which are critical in obtaining good glasses.

6. It was demonstrated that high temperature superconductors in both the Y-Ba-Cu-O and Bi-Ca-Sr-Cu-O systems could be formed by wet chemical routes. The preferred synthesis route involved the use of nitrate solutions. Critical temperatures for superconducting behavior similar to those of the best vapor-deposited films were demonstrated. The approach has significant commercial potential, and a patent disclosure was filed.

7. For a range of compositions in the Bi-Ca-Sr-Cu-O systems, it was demonstrated that glasses could be formed. The ability to form glasses was related to chemistry and knowledge of the kinetic processes involved in glass formation. The crystallization behavior of the glasses was determined, and superconductivity of the resulting crystallized bodies was demonstrated.

8. Using wet chemical synthesis routes based on sol-gel methods, barrier layers having a broad range of chemistries were prepared; and their effectiveness as barriers to interaction between superconducting films and substrates was evaluated. Improvement in critical temperature for superconductivity through the use of such barrier layers was demonstrated.

I.   INTRODUCTION AND PERSONNEL

The present program was started at MIT, and was transferred to the University of Arizona with the principal investigator, Professor Uhlmann. It was initiated to explore the feasibility of wet chemical (sol-gel) methods for the synthesis of heavy metal fluoride glasses. It also was concerned with a novel approach to passivating the surfaces of such glasses against attack by atmospheric moisture. During the third year of the program, the phenomenon of high temperature superconductivity in ceramic oxides burst upon the technical scene. At the suggestion of our technical monitor, Dr. Ulrich, we redirected our research efforts under the program to explore the chemical synthesis of oxide superconductors, the formation of glasses of such superconductors and their subsequent crystallization behavior, and the chemical synthesis of barrier layers for use with superconducting thin films (to reduce interactions between the superconducting layers and the substrates on which they are formed). In the work on high temperature superconductors, personnel from the present program worked as a team with personnel from our AFOSR-sponsored program on ceramics from metal-organic precursors; and the results reported below represent in this area an amalgam of the two programs.

The work on synthesis and passivation of fluoride glasses was carried out by Ms. M. Andersen and Messrs. G. Teowee and G. Dale. After completing her studies at MIT, Ms. Andersen joined private industry; and Messrs. Teowee and Dale are presently completing research toward the Ph.D. degree at the University of Arizona. In the work on high temperature superconductors, Messrs. Teowee and

Dale were joined by Mr. Matthew Denesuk, a graduate student presently working toward the Ph.D. degree in the Department, and a number of part-time undergraduate researchers, Messrs. G. Berry, M. Choudry, T. Gudgel and M. Smith and Miss K. Hamm. Besides producing valuable data for the program at minimal cost, the undergraduates obtained hands-on experience in the carrying-out of original research.

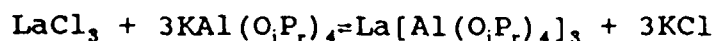## II. RESEARCH REPORT, FLUORIDE GLASSES

The activity directed to fluoride glasses was concerned with three general areas: (1) wet chemical synthesis of heavy metal fluoride glasses; (2) modelling of crystallization in a glass body formed by cooling to a glass, reheating to a draw temperature and cooling again to a glass; and (3) surface treatment of fluoride glasses to increase their durability.

In work on the wet chemical synthesis of fluoride glasses, attention was focused on the synthesis of multi-component oxide gels as precursors for the fluorides and on the synthesis of high purity fluorides of individual cations. It was found in our early work that when attempts are made to produce oxide gels of precursors for heavy metal fluoride glasses by hydrolysis and condensation of simple mixtures of alkoxides, chemical inhomogeneity generally results and solubility problems are encountered with the alkaline earth species.

Attention was therefore focused on the synthesis of double alkoxides containing the desired cation species; and preliminary effort was also directed to the synthesis of multialkoxides containing more than two cations. The double alkoxides synthesized during the program include:
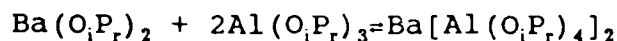
1. Lanthanum aluminum isopropoxide, synthesized from lanthanum chloride and potassium aluminum isopropoxide. That is

$$LaCl_3 + 3KAl(O_iP_r)_4 = La[Al(O_iP_r)_4]_3 + 3KCl$$

This synthetic route was found to be effective in producing the desired double alkoxide, even without using a catalyst.

2. Barium aluminum isopropoxide, synthesized from barium isopropoxide and aluminum isopropoxide using $HgCl_2$ as a catalyst. That is

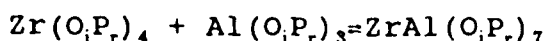$$Ba(O_iP_r)_2 + 2Al(O_iP_r)_3 = Ba[Al(O_iP_r)_4]_2$$

In this case, the synthesis route followed that initially reported by Bradley and his co-workers.

3. Barium zirconium isopropoxide, synthesized from barium isopropoxide and zirconium isopropoxide, also using $HgCl_2$ as a catalyst. That is

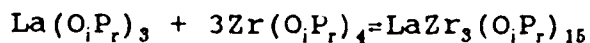$$Ba(O_iP_r)_2 + 2Zr(O_iP_r)_4 = BaZr_2(O_iP_r)_{10}$$

Again the synthesis route proved to be successful in yielding useful quantities of the double alkoxide.

4. Zirconium aluminum isopropoxide, synthesized from zirconium isopropoxide and aluminum isopropoxide. That is

$$Zr(O_iP_r)_4 + Al(O_iP_r)_3 = ZrAl(O_iP_r)_7$$

This synthesis was also carried out using $HgCl_2$ as a catalyst.

5. Lanthanum zirconium isopropoxide, synthesized from lanthanum isopropoxide and zirconium isopropoxide. That is

$$La(O_iP_r)_3 + 3Zr(O_iP_r)_4 = LaZr_3(O_iP_r)_{15}$$

Again, $HgCl_2$ was used as a catalyst.

Following synthesis of the double alkoxides, effort was directed to characterizing their hydrolysis and condensation behavior, particularly of the first three (lanthanum aluminum, barium aluminum and barium zirconium isopropoxides). The combination of these double alkoxides provides the basis of synthesizing a number of ZBLA glasses. In all cases, the hydrolysis and condensation were carried out using isopropanal as a solvent. Both direct additions of water-isopropanal solutions and in-situ generation of water have been explored. In the latter use, the water was generated by adding an organic acid (acetic acid) to the alcohol at controlled elevated temperatures.

Of the three double alkoxides, the barium zirconium isopropoxide displayed the most rapid reaction kinetics. Hence in work directed to forming oxide gels of the four constituents, preliminary partial hydrolysis of the lanthanum aluminum and barium aluminum isopropoxides was carried out. Different degrees of preliminary partial hydrolysis were required for the two non-zirconium-containing alkoxides; and work was initiated to determine the conditions for effecting the desired polycondensation (including variations in temperature during polymerization of the type we had previously found to be important in synthesizing chemically homogeneous cordierite). Because of the shift in emphasis to high temperature superconductors during the third year of the program, this phase of the investigation was not completed.

The program did, however, demonstrate the formation of a number of multicomponent gels containing Zr+Ba, Zr+Ba+La, Zr+Ba+La+Al. In all cases, isopropanol was used as a solvent; in

some cases, acetyl acetonate was employed as a complexing agent and found to help keep intermediate species in solution during hydrolysis and condensation. The starting (precursor) materials consisted of the double alkoxides discussed above, as well as zirconium isopropoxide and in some cases salts of the metal cations. It was gratifying to find that gels could readily be prepared over a wide range of composition. The volume fraction solids of the materials as-gelled was in the range of 10-20 pct.

After drying to remove the isopropanol, the gels were fluoridated at temperatures between 300 and 550°C. The fluoridations were carried out in a furnace fitted with an inconel tube. The reactive gas used as CF_3Cl, which is a liquid at room temperature. Gas flow was effected by heating a closed container of the liquid and leading the gas through the furnace. Elemental analysis of the fluoridated products indicated that the conversion was nearly complete, with some Cl also present. Depending on the time and temperature of the treatment, the products ranged from shiny, brittle black particles to deliquescent yellow particles. The latter were shown by X-ray diffraction to consist of crystalline ZrF_4.

It is expected that lower temperature fluoridation treatments would be effective in preventing crystallization. Such treatments, which would involve the use of more reactive gases such as fluorine or HF, should also permit the gels to remain intact as solid bodies rather than be comminuted during the course of the reaction. The comminution products would, however, be valuable as novel high purity fluorides for preparing glasses by melting.

In general, then, it was found that gels containing heavy metal cations to serve as precursors for corresponding fluoride glasses could reliably and reproducibly be formed. These gels could be fluoridated with success; and it appears that the fluoridation process merely needs optimization.

Effort was also directed to using sol-gel methods to produce high purity precursors (and eventually high purity fluoride glasses). In this work, high purity single alkoxides and double alkoxides of heavy metal cations were prepared by multiple fractional distillation, and in preliminary studies by multiple fractional crystallization. The results which were obtained were quite encouraging: even starting from highly impure alkoxides, it was possible to obtain alkoxides of high purity (reductions in impurity contents exceeding two orders of magnitude were routinely obtained), and from these to obtain high purity gels.

In other phases of the investigation of fluoride glasses, attention was directed to two areas: (1) modelling the development of crystallinity in a body subject to a thermal history of cooling to a glass, heating to a draw temperature and cooling again to a glass; and (2) exploring the use of surface treatments of fluoride glasses to increase their durability.

In the modelling work, two different cooling rates were considered within the framework of the analysis of crystallization statistics, an analysis previously developed by our research group which has been used with success to describe the crystallization

which takes place on reheating a glass as a function of material characteristics. To accomplish the description of recooling after reheating, a rewriting of existing computer programs and their combination into a master code were undertaken; and introduction of a third stage of thermal history was included. With the new code, it is possible to describe the number and size distribution of crystallites in an amorphous body subject to an arbitrary cooling-heating-cooling thermal history. That is, the computer code provides a detailed description of crystallization of a liquid body which is cooled to below the glass transitions (Tg) at an arbitrary rate R_1, then reheated at an arbitrary rate R_2 to a temperature T_2 above the glass transition (where the body may be shaped, as drawn into a fiber), and subsequently cooled at an arbitrary rate R_3 to below Tg.

With this code in hand, work was initiated to describe the effects of changes in material characteristics on the ability to form glassy fibers, free of small crystalline inclusions. Included in the material characteristics which were explored are the melt viscosity as a function of temperature, the liquidus temperature, the crystal-liquid surface free energy and the heat of fusion.

Such calculations have indicated that the crystallization which takes place during the reheat stage depends upon the percent crystallinity in the initially-formed glass, at least for volume fractions of crystallinity which exceed about 10^{-10}. That is, the degree of crystallinity in the as-formed glass affects the stability of the liquid against crystallization during subsequent heating above the glass transition temperature, save when the

percent crystallinity in the as-formed glass is very small (less than about 10^{-10}). These results suggest that very rapid cooling to form the initial glass - employing cooling rates which well exceed the minimum cooling rates for glass formation - should be advantageous for enhancing the resistance to crystallization on subsequent reheating.

The calculations also indicate that the draw temperature and the temperature intervals among the draw temperature, liquidus temperature and glass transition temperature are important in affecting the degree of crystallization which will occur in the finally cooled glass bodies (fibers in the case of present interest).

In a separate, chemistry-based activity concerned with fluoride glasses, attention was directed to providing passivation to fluoride glasses (increasing their resistance to chemical attack by species such as water) by reacting their surfaces to form durable compounds. The bases for this activity were the facts that fluoride glasses suffer severely from interaction with water, that the surfaces of such glasses can be reacted under reasonable conditions with sources of other anions leaving the bulk of the glass unaffected, that the reaction products can be bonded effectively to the base glass, and that suitably selected reaction products are characterized by greatly reduced rates of attack by water compared with the base glass. With respect to fluoride glass fibers, only the outermost surface region of the cladding need be

reacted, thereby leaving unaffected the optical performance of the fibers.

In work carried out during the program, sulfate ions were selected for exploration of the concept. By converting heavy metal fluorides to heavy metal sulfates, a considerable decrease in the solubility in water could be effected (e.g., while barium fluoride is highly soluble in water, barium sulfate is substantially insoluble). Similar decreases in solubility are found, albeit to different degrees, for other cations which are important in heavy metal fluoride glasses.

Sulfates were formed on the surfaces of representative ZBLA glasses by reacting them with concentrated sulfuric acid. The reaction was found to take place readily even at room temperature, and was explored over a range of temperature from subambient to the boiling point of sulfuric acid. The morphology of the reaction product layers was found to depend on the temperature of reaction, with more uniform layers being produced at lower temperatures.

Bulk ZBLA glasses with reaction layers on their surfaces were immersed in water for various times and temperatures at various pH's. The surface corrosion process for the reaction-coated glasses was found to display diffusion-controlled kinetics. Of particular note and as expected, the rate of corrosion at any time was considerably decreased compared with that of the unreacted glass. Decreases in corrosion rate exceeding a factor of 3 were routinely obtained, and decreases of an order of magnitude were found in some cases. Given the exploratory nature of the investigation, such decreases in corrosion rate should not be taken

as the limits of achievable passivation; and much larger decreases should be achievable by optimizing the reaction process.

The results obtained in this area are encouraging, and represent an interesting example of the chemical modification of materials to improve their performance in critical respects. Promising extensions of the work would include characterization of the reaction products on the scale of ultrastructure, tailoring of the reaction process to the glass composition, and evaluating the strengths of heavy metal fluoride glasses both before and after the reaction and following exposure to water for different periods of time.

III. RESEARCH REPORT, HIGH TEMPERATURE SUPERCONDUCTORS

As indicated in the Introduction, the research activity concerned with high temperature superconductors was directed to three principal areas. These are (1) wet chemical synthesis of high temperature superconductors, (2) the formation of glasses of high temperature superconductors and their subsequent crystallization behavior, and (3) chemical synthesis of barrier layers for use with superconducting thin films.

A. Wet Chemical Synthesis of High Temperature Superconductors

The discovery of superconductivity at temperatures above liquid nitrogen temperature has opened up new vistas of possible industrial application. Processing of thin films is a very important step in many technological exploitations of these superconducting materials. The techniques for depositing superconducting films on various substrates comprise electron beam evaporation, molecular beam epitaxy, sputtering and pulsed laser evaporation. These techniques invariably require high vacuum (as $10^{-6} - 10_{-7}$ Torr) and expensive equipment. The superconductive transitions that have been reported in these studies are generally in the range $60° - 95°K$ depending on the type of substrate and the firing and annealing procedures employed.

The high vacuum conditions required for the existing techniques for depositing superconducting films require skilled operators. The evaporation or sputtering targets have to be prepared in the form of alloys which are expensive to prepare. Moreover, it is economically unattractive to coat large and intricate objects with these techniques. These problems can be

overcome by wet chemical processing which involve inexpensive machinery and relatively unskilled operators.

Prior to the present work, there was one unsuccessful attempt to process superconducting films on ceramic substrates by spraying solutions of yttrium, barium and copper compounds. Attempts to measure the resistivity of the annealed films were unsuccessful because the films were extensively cracked. In other words, superconductivity was not observed; and a continuous film, covering the surface of the substrate, was not achieved.

In the present work, techniques have been developed for processing homogeneous films by spraying or otherwise depositing nitrate solutions of cation combinations such as Y, Ba and Cu or Bi, Sr, Ca, Cu or ceramic substrates. After firing, the resulting oxide films exhibit superconductivity up to temperatures similar to those of films obtained by vacuum deposition techniques.

The cations, preferably in the stoichiometric ratio (e.g., for the Y-Ba-Cu system, the ratio is 1,2,3) are incorporated in a clear solution. The solution can be aqueous, whether acidic, neutral or basic. Compounds, such as the oxides, nitrates, carbonates or hydroxides or a combination of these, can be dissolved in acids or water. Mild heating associated with stirring may be necessary to obtain a clear solution. It is beneficial to have a saturated solution, but care must be taken to ensure that no precipitate is formed.

The substrate can be a metal, a ceramic or a glass. The substrates should be cleaned and heated to a suitable temperature such that a drop of solution will evaporate relatively rapidly on

contact. There exists an optimum temperature range for a substrate-solution combination which facilitates formation of a good film. For the Y-Ba-Cu (1,2,3) system, this temperature range is 170-190°C; and for the Bi-Sr-Ca-Cu (4,3,3,4) system, the temperature range is 210-230°C. An unduly low substrate temperature results in a wet film, and the desire stoichiometry is difficult to maintain. The less soluble components tend to precipitate, whereas the more soluble components tend to remain in solution and tend to get washed away during successive depositions. Moreover, problems arising from local non-stoichiometry arise if an unduly low substrate temperature is used. An unduly high substrate temperature has also been found to result in defective films which are patchy in texture and may contain numerous cracks.

Several methods of depositing films have ben employed. These include:

Technique I: The deposition of the film may be carried out by depositing the solution onto hot substrates in the form of small drops. The substrate is kept flat on a heat source such as a hot plate, and drops of the solution are added at regular intervals to the substrate. The liquids spread over the substrate on contact and dries rapidly, leaving a film on the substrate. The number of drops required to form a film depends on the surface area of the substrate, the solute concentration of the solution and the size of the drop.

Technique II: Solutions may be sprayed with a spray gun onto suitable substrates, the surfaces of which are heated and maintained at a pre-determined temperature. The substrate is kept

flat on a hot plate, and spraying is preferably done from a point located vertically on top of the substrate. To prevent loss of the more soluble components, spraying is preferably performed intermittently, making sure the already deposited film is at the pre-determined high temperature. The number of spraying cycles which is required depends on parameters such as the type of spray gun, the area of the substrate being coated, the concentration of the solution and the film thickness required.

Technique III: An assembly of spray guns may be positioned on the periphery of a circle and the substrate is placed at its center. A heating device heats the substrate to a desired temperature and all the sprayers are activated at the same time. Spraying from all directions will ensure the desired stoichiometry of the film being processed. The number of spray guns will be determined by the area of the substrate.

Technique IV: Spraying a small substrate from a vertical direction may entail some loss of solution. To reduce this wastage, a guard wall around the substrate may be placed. The sprayer is positioned at the top opening of the guard well, and spraying in this configuration will minimize wastage of the solution.

A number of other deposition techniques such as dip-coating, ultrasonic spraying, and roller-coating may also be used to good effect.

The films deposited by any of these techniques are ready to be fired immediately thereafter. The firing may conveniently be carried out in horizontal tube furnaces, but other furnace

geometries may be used as well. The furnaces should have attachments for flowing oxygen gas during the heat treatment. Each superconducting system has its own firing and annealing schedules. These depend on the chemical composition of the oxides as well as the physical and chemical nature of the respective superconducting phases.

In general, slow heating rates are desired to allow the film and the substrate to adjust to the thermal expansion mismatch. An extended soaking period from 400° to 620°C seems important because in this temperature range the gases resulting from the decomposition of the nitrates evolve. Sintering of Y-Ba-Cu films starts at temperatures in the range of 650°C. If all the gaseous products of nitrate decomposition are not allowed to diffuse away from the film, the porosity of the film may increase, resulting in increased resistivities of the samples. A prolonged soaking at 880°C facilitates improved sintering of the film, giving it a good connective texture. The films are black in color and no cracks or apparent defects are observed.

For systems other than Y-Ba-Cu or for starting materials other than nitrates, the temperature range at which the starting compounds decompose can readily be determined; and a soak in that temperature range should be allowed. Similarly, the highest sintering temperature and the subsequent annealing range of temperature should be tailored for each superconducting system.

Standard four-probe electrical measurements were performed on the films. Silver electrodes were pasted on the film with silver paint. A representative resistance vs. temperature plot for a

$YBa_2Cu_3O_7$ film is shown in Figure 1 on the following page. The critical temperature is observed to be $94°K$. X-ray diffraction studies using $CuK\alpha$ radiation were performed on the films. The variation of intensity with scattering angle indicated that the majority phase in the film was $YBa_2Cu_3O_7$.

In the case of Bi-Sr-Ca-Cu-O (4-3-3-4) films deposited on partially stabilized zirconia substrates, black films, without any apparent cracks or pores, were formed (similar in appearance to the Y-Ba-Cu-O films). Standard four-probe electrical measurements showed that these films were superconducting and that their critical temperatures were in the range of $85°K$.

It has thus been demonstrated that it is possible using wet chemical synthesis routes to produce dense, crack-free films with superconducting critical temperatures similar to those of the best vapor-deposited films. The wet chemical route offers great potential for highly cost-effective processing; and the critical issue for its wide-scale implementation is that of critical current density, which is presently being addressed in another context in a separate Air Force-sponsored program. Because of the technological potential of the wet chemical route to high temperature superconductors, a patent disclosure has been prepared and filed with the University patent section.

B. Glass Formation and Crystallization Behavior of High Temperature Superconductors

In our exploration of processing techniques which offer important potential for cost-efficient synthesis of high

temperature ceramic superconductors, attention was also directed to melt processing. It was recognized that melt processing techniques are potentially very interesting because, in principle, they can be used to fabricate complex geometries, such as wires, films and odd-shaped articles. They also can provide great flexibility for microstructural control, as well as for enhancing properties through chemical homogeneity.

In the present work, attention was focused on glass formation and crystallization behavior as a function of composition and thermal history in the Bi-Ca-Sr-Cu-O system. The system was selected for detailed investigation because of the attractive high temperature superconducting characteristics of several Bi-Ca-Sr-Cu compositions, and because preliminary exploration in our laboratory demonstrated the surprising result that several of the compositions were reasonable glass-formers.

Four different compositions in the Bi-Ca-Sr-Cu-O system, with compositions 2122, 2223, 4334 and 4223, were melted in Al_2O_3 or Pt crucibles at temperatures varying from 1050C to 1200C for 15 minutes. The number indicate the atomic compositions of Bi, Ca, Sr and Cu. Further designations A and P refer to samples melted in Al_2O_3 and Pt crucibles respectively.

The batch materials were reagent grade Bi_2O_3, $CaCO_3$, $SrCO_3$, $Sr(NO_3)_2$ and CuO. The first three compositions were chosen based on reports which identify two superconducting phases in the new system: the T_c=110K phase (2223) and the T_c=85K phase (2122). Both of these phases could not be obtained in isolation by sintering powders having the exact stoichiometric compositions, the

recommended starting composition being 4334. In the present work, we attempted to make glasses and subsequently to crystallize single phase HTSC materials. The fourth composition, 4223, was made in order to test the effect of Bi on glass formation in this system.

The melts were very fluid and highly corrosive, and hence a substantial amount of Al is expected to be dissolved in the liquid when melting is carried out in Al_2O_3 crucibles. Composition 2223P was melted in a Pt crucible and no sign of chemical attack was observed. In this case, $Sr(NO_3)$ was used instead of $SrCO_3$ to prevent reduction of Bi and consequent alloying with Pt.

The liquids were cast on graphite molds or quenched between two steel plates. The thickness of the as-cast plates was typically about 1 cm. Table I summarizes the compositions investigated and the rough glass-formability of the materials melted and cooled in different ways. For purposes of this table, the glass yield is defined as the thickness of the bottom layer (which first touched the mold on casting) and appeared glassy to the eye. It should be noted, however, that SEM observations and X-ray diffraction analysis have shown a small degree of crystallinity in the "glassy" layers of the cast 2223 and 4334 compositions. The glassy layers in the 2122 and 4223 samples were X-ray amorphous.

The heat treatments were carried out in a muffle furnace. The specimens were inserted into the cool furnace which was then slowly heated to the desired temperature, between 845C and 885C; and held at that temperature for periods of up to 40 hours. After the holding periods, the specimens were allowed to cool inside the

furnace. In some cases, an optical microscope provided with a hot stage was used to carry out heat treatments.

The resulting microstructures were analyzed by optical and scanning electron microscopy, as well as by X-ray diffraction. Four probe d.c. electrical measurements were performed by the linear 4-point and the Van de Paun configurations. A current of 1 mA was used during the measurement. Silver paste was used to attach indium leads to the samples.

The as-cast 2122 material, having a thickness of about 1 cm., was glassy in appearance (no evidence was found for internal crystals visible at magnifications of 100-200X), save for a thin skin on the top surface (the melt-vapor interface). This surface skin had crystalline material, was typically less than 0.1 mm in thickness, and was also observed on much thinner samples (samples whose thickness was in the range of 1 mm). No such crystalline skin was found on the surfaces which had been in contact with the graphite mold. X-ray diffraction of the bulk of the cast material indicated only a broad diffraction maximum typical of an amorphous material.

When placed in a furnace provided with an oxygen atmosphere and maintained at 865°C, the samples were observed to crystallized completely in periods of less than 1 hour. During such times, pronounced slumping of the samples was observed. In addition, marked evolution of gas took place during such crystallization treatments, presumably from the raw materials used in preparing the original melts. This evolution of gas produced a pumice-like appearance of the samples.

X-ray diffraction analysis of the crystallized samples indicated that an important crystallization product was the second phase(s) seen in crystallized samples of the (2223) and (4334) compositions - see below - rather than the expected dominance of the tetragonal (2122) phase. There was, however, a significant fraction of the tetragonal (2122) phase included in the body.

The resistance vs. temperature relation for material crystallized at 865°C for 1 hour indicated a sharp drop in resistance over the temperature range 133-91°K, but the condition of zero resistance was not achieved at temperatures above 91°K (see Figure 2).

When the as-cast material ws remelted in a Pt crucible at 900C, gas evolution was complete within 15 minutes. When the temperature was lowered to 865°C and maintained at that temperature for 10 minutes, complete crystallization of the sample was observed. In this case, however, the sample had a monolithic character, without the presence of large numbers of gas bubbles. X-ray diffraction of this body indicated the presence of only the other phases(s) seen in crystallized samples of (2223) or (4334) composition. No diffraction peaks were seen which corresponded to the (2122) phase.

The resistance vs. temperature relation for this remelted and crystallized material is presented in Figure 3. As shown there, a sharp drop in resistance with decreasing temperature, beginning at about 103°K, is observed. The state of zero resistance is, however, not observed at temperatures above 87°K.

SEM observations of 2223 material which had been melted in Al_2O_3 crucibles and cast of the same material melted in Pt crucibles rapidly quenched between steel plates showed a notably greater thickness of the "glassy" layer in the sample melted in the Al_2O_3 crucible - despite the more rapid cooling used with the sample melted in Pt. The "glassy" regions were seen to contain a few small crystals, which appear to be associated with bubbles (seed) in the material. These crystals were identified by X-ray diffraction as consisting entirely of the 2122 phase. The crystalline top surface regions in these as-cooled specimens consist of plate-shaped crystals as well as a matte-appearing second phase. X-ray diffraction confirmed the presence of two phases.

After subsequent heat treatment of the "glassy" 2223 material to produce crystallization, the presence of micaceous (plate-like) crystals was clearly seen, as are crystals of a second, matte-appearing phase.

Observations of cast samples of the 4334 material which had been melted in Al_2O_3 indicated a "glassy" layer which is larger than that in the 2223 material. As with the 2223A samples, some small crystals are seen in the "glassy" regions; and these crystals are the 2122 phase. The crystalline regions again consist of two phases, one of which is the plate-like in appearance and which was identified by diffraction as the 2122 phase.

When heated in an oxygen atmosphere while viewed in an optical microscope, crystallization of the "glassy" 2223A material was observed to occur rapidly at temperatures in the range of 850°C

(growth rates were in the range of mm/sec). On further heating, partial melting was observed in the range of 925°C. At higher temperatures, none of the plate-like crystals were seen; but the matte-appearing fine-grained crystals persisted until temperatures approaching 1200°C.

By comparison, the 2223P material was observed to crystallize in periods as short as 10 sec. at temperatures in the range of 860-870°C. On further increasing of the temperature, melting was observed to begin at about 890°C; and by about 1050°C, the sample was molten save for a small volume fraction of the matte-appearing phase. This phase persisted to temperatures above 1220°C.

Figure 4 shows the relative resistances of composition 2223A (initially "glassy") which had been heat treated respectively at 845°C for 4 hours, 865°C for 40 hours and at 860°C for 28 hours. The absolute values of the resistance at 273°K (for similar geometries) were typically 0.02, 0.004 and 0.12 (arbitrary units), respectively. The as-cast "glassy" specimen had a resistance of 24. Hence, there is a difference of 4 orders of magnitude between the least and the most resistive specimens at 273°K. The resistivity at 300°K of sample 2223A heated at 840°C is 5700 Ω-cm.

Figure 4 also shows the dramatic changes in behavior caused by different heat treatments. For treatment at 845°C, a metallic behavior is observed, with a superconductive onset at T_{on} = 110°K, although zero-resistance behavior was not detected at temperatures above 85°K. With a long treatment (40 hours) at 865°C, the specimen warped slightly and was dark black. The resistance drops continuously with decreasing temperature and undergoes a clear

transition with $T_c = 85°K$. The "anomaly" reported by several authors between 110°K and 120°K is clearly seen and indicates the presence of another superconducting phase. When the "glassy" specimen is heated at 885°C, it partially melts, a shiny surface is obtained, and it fails to exhibit superconducting behavior, at least at temperatures down to 85°K.

Figure 5 shows the relative resistance plots for three different compositions (2223A, 2223Pt and 2223B) heated to 865°C for several hours. Sample 2223A was melted in a rather porous Al_2O_3 crucible, while sample 2223B was melted in an impervious Al_2O_3 crucible. The amount of attack on the crucible by the melt was much greater for 2223A than for 2223B. In spite of the differences in chemical compositions (different Al_2O_3 contents), they all show metallic behavior and have zero resistance at approximately 85°K.

Figure 6 shows the relative resistances of composition 4334 as-quenched (crystalline side) and heated to 845°C for 4 hours and to 875°C for 2 hours. Both as-quenched sides ("glassy" and crystalline) do not superconduct down to 10°K. The glassy layer has a much higher resistance and is not shown in the graph. The "glassy" specimen heated to 845°C has a much lower resistance which does not vary significantly down to 85°K. The "glassy" specimen heated to 875°C shows a superconducting onset at about 110°K, but did not superconduct at temperatures above 85°K.

The present work has demonstrated that melting, quenching and subsequent crystallization plus annealing provides a useful alternative route to powder or vapor-phase processing for forming superconducting Bi-Ca-Sr-Cu-O materials. The present results

provide support for such processing as an attractive route to forming high-T_c superconductors in useful shapes. This route offers the attractive features which accompany liquid state processing.

A significant aspect of the present study is the ability to quench the liquid into the glassy state. In this regard, it was found that the incorporation of Al_2O_3 in the 2223 melt has a clearly beneficial effect in promoting glass formation without deleteriously affecting the critical temperature for superconducting behavior. Similar beneficial effects of Al_2O_3 on glass formability are expected for the other Bi-Ca-Sr-Cu-O compositions as well. In the work reported here, the Al_2O_3 was obtained by partial dissolution of the crucible in the melt; but in on-going work, it is provided by additions to the batch. The effect of such additions on critical current density also needs clarification.

Considering the high fluidity of these melts at temperatures near the liquidus (they pour rather like water), it is remarkable that they can be formed as substantially amorphous materials by simple casting. This likely reflects a sizable barrier to crystal nucleation and/or a large temperature dependence of the viscosity – or alternatively a relatively small interval between the upper temperature limit of stability of the 2122 phase ($T_{L'}$) and the glass transition temperature (T_g). Based on observations of the cast/quenched specimens, it appears that the matte-appearing phase on the liquidus is not the first to nucleate on cooling. Rather, it is the 2122 phase, which presumably reflects its smaller

crystal-melt interfacial energy. On this basis, the relative factor in considering glass formation is not $T_{liquidus} - T_g$, but rather $T_{L'} - T_g$.

The addition of Al_2O_3 has only a modest effect on the viscosity at a given temperature (judging from the pouring behavior). The effect of Al_2O_3 on glass formability must then be related to its role in reducing $T_{L'}$ and/or the crystal-melt interfacial energy, or in decreasing the crystal growth rate via its effect on the interdiffusion coefficient in the melt.

The observation of small crystals associated with pores in the "glassy" cast material very likely reflects nucleation on second-phase impurities, rather than simply on the liquid-vapor interfaces of the pore surfaces. The nature of the suggested second-phase impurities remains to be identified. The subsequent crystallization of such "glassy" material is being further investigated to elucidate the role of the observed crystallites and thermal history of the glass.

It is noteworthy that X-ray diffraction of the "glassy" material in both the 2223 and 4334 samples indicates the presence of a small amount of only the 2122 phase (the phase suggested as responsible for high temperature superconducting behavior). After complete crystallization, however, both samples show the presence of two crystalline phases with distinctive morphologies. The crystallization process as observed in the optical microscope took place too rapidly to permit detailed observation of the sequence of phase development, but presumably growth of the small 2122

crystals present in the "glassy" material was accompanied/followed by nucleation and growth of the matte phase.

Based on the present observations, it appears that the preferred heat treatment schedules in the literature for preparing superconducting samples of the 2223 and 4334 compositions involve partial melting of the 2122 phase. In particular, it appears that these heat treatments involve a reorganization via dissolution/re-precipitation, which may involve some increase in the volume fraction of the 2223 phase at the expense of the 2122 phase, but almost certainly involves the development of more favorable interconnected morphologies of the preferred phase(s).

The times required for complete crystallization of the samples at 865°C are much shorther than the heat treatment times used to prepare the superconducting samples (less than a minute vs. several hours).

It appears that superconducting material of the 2223 composition can only be prepared by crystallization in a narrow range of temperature (845C<T<885C). The origin of this behavior is not satisfactorily understood at the present time, but must involve the development of different phase assemblages/microstructures at the different temperatures. X-ray diffraction indicates a similar distribution of diffraction peaks in material crystallized at 865°C. Also of note is the marked difference in conductivity behavior over the temperature range 275K-125°K among glasses crystallized at 845°C, 865°C, and 885°C.

Regardless of the details of the crystallization process, it appears that extended heat treatments - much longer than those

required to develop a substantial degree of crystallinity - are required to obtain superconducting samples. Whether these extended heat treatments are required for reasons of oxygen stoichiometry, or for the development of appropriate crystalline-phase assemblages, is presently being explored.

C.   Wet Chemical Synthesis of Barrier Layers

It is well established that substrate composition and orientation play crucial roles in determining the properties of thin film ceramic superconductors. The substrate can affect both the epitaxial quality of the superconductor coating and interdiffusion between the substrate and coating; these, in turn, affect superconducting properties (e.g., transition temperature and critical current density).

The importance of substrate diffusion in thin film ceramic superconductor has inspired many investigators to coat the substrates with barrier layers, in the hope of effectively separating the coating from the diffusing substrate cations. ZrO_2, SiO_2, Ta_2O_5, LaF_3, MgO, VN, $La_2O_3 \cdot Al_2O_3$, Ag, Au (and some other compositions) have been tried. Many of these coatings -- especially ZrO_2, Ag, and Au -- have resulted in significant improvements in the electrical properties of ceramic superconductor coatings. In general, these barrier layers have been used with superconductor coatings which are applied by vacuum deposition techniques, such as magnetron sputtering, evaporation, and electron beam evaporation. As a result, the barrier layers have also been deposited using high vacuum processes. For chemically derived

superconducting coatings, however, the advantages in cost and versatility would be lost if the substrates had to be first coated with a barrier layer in a vacuum chamber. Hence, there is a need to develop barrier layers which can be deposited by more simple, versatile techniques, such as wet-chemical, or sol-gel, techniques.

In initial work under the program, wet chemical methods were used to deposit ZrO_2 barrier layers on sapphire substrates. Onto such coated substrates, a second barrier layer of Ag was deposited. This combination allowed superconducting $YBa_2Cu_3O_{7-x}$ films to be sputter-deposited on sapphire. Without the barrier layer, the films were not superconducting; and with the composite barrier layer, a T_c onset of 89°K with a T_c completion of 65°K was observed.

In subsequent work, we investigated a broader range of sol-gel barrier layers. These include Ta_2O_5, since it forms a nominally dense sol-gel coating at low temperatures (450-500C); Y-stabilized ZrO_2 (YSZ), which is one of the preferred bulk substrate materials and which (without yttria stabilization) is a commonly used vacuum deposition barrier lyaer; $Y_2Cu_6O_9$, which may provide not only a barrier layer but also serve as a source of excess copper, which is often deficient after heat treatments; and $BaTiO_3$ and $SrTiO_3$, which were studied because of the superiority of $SrTiO_3$ as a bulk substrate material. Each barrier layer was investigated with and without silver overcoats.

Results reported to date under the program included the development of synthesis procedures for two of these barrier layers (Ta_2O_5 and Y-stabilized ZrO_2) as well as the effects of these barrier layers on coating adhesion, coating/substrate

interdiffusion, and resistivity measurements for $YBa_2Cu_3O_{7-x}$ films sprayed from nitrate solutions onto barrier-coated sapphire substrates.

Barrier Layer Synthesis

The coating solutions were made from alkoxide precursors. All solvents were purified by standard procedures before use. Single crystal sapphire slides, 90° cut (1cm x 1cm x 1mm) were used as the substrate material. The slides were cleaned using the Huang process before coating. All samples were coated using a spin coater, 2000 rpm, for 20 sec.

Ta_2O_5 coatings were obtained from $Ta(OCH_2H_5)_5$ solutions. A 5 wt% $Ta(OCH_2H_5)_5$ solution in dry ethyl alcohol was prepared in a three-neck flask equipped with a nitrogen inlet, condenser, drying tube, and stirring and heating accessories. Water was added to this solution so as to maintain a 1:1.3 water to alkoxide ratio. The solution was stirred at room temperature for one hour, and then coated onto the sapphire substrates. To increase the thickness, this coating was heated at 80C for 10 minutes, and then a second Ta_2O_5 layer was spun on. The dual coatings were finally fired for 4 hours at 950C in air. Rutherford Backscattering (RBS) analysis showed the resulting coatings to be ~600 Å thick.

To prepare Y-stabilized ZrO_2 barrier layers, zirconium n-propoxide and anhydrous yttrium chloride were weighed into a three-neck flask, equipped as described above. The weight of components was adjusted in such a way that ZrO_2 containing 9 wt% Y_2O_3 would be obtained. Dry isopropyl alcohol (30 ml) was added to this solution, and the resulting mixture was heated until a solution

free from any solid particles was obtained. To hydrolize the alkoxide mixture, 1 mole% of the amount of water required for complete hydrolysis was added to one ml isopropyl alcohol. This hydrolysis solution was then added the the alkoxide solution and refluxed for about five hours. The solution was then spin coated onto the pre-cleaned sapphire substrates. A second coating was deposited after the first had been fired at 400°C in air for one hour. Then, the dual coating was given a final heat treatment at 900°C for four hours. RBS analysis showed the product coating to be ~800 Å thick, and X-ray diffraction analysis showed the coating to be a cubic crystalline phase.

Superconductor Coatings

Y-Ba-Cu-O films were sprayed onto the barrier layers using a nitrate solution technique which was described in detail above. Basically, the process involves mixing nitrate solutions of the cations in the stoichiometric ratio (1:2:3 Y:Ba:Cu) and spraying this solution onto heated (170-190°) substrates. The sprayed coatings were then given a complicated heat treatment, part of which involved heating at 925°C for 6 hours. The details of the spraying procedure and firing schedule are both important in obtaining good superconducting properties.

For 15 μm coatings sprayed on bulk yttria-stabilized zirconia substrates, a superconducting onset is obtained at 94K, with a transition width of about 12°K (zero resistivity at 82°K). For thinner coatings, the onset temperature decreases and the transition width increases. It is apparent, therefore, that the

extent of substrate poisoning can be very large -- i.e., microns in extent -- with the nitrate-derived coatings.

Coating Adherence

For bulk YSZ substrates, the nitrate deposition technique formed very robust, well adhering coatings. When the oxide barrier layers were added, the coatings became somewhat more fragile, and could be partially scraped off with a razor blade. In our previous work on sputtered films, no such effect was observed with the sol-gel barrier layers. It is apparent that the complex chemical interactions at the coating/substrate interface make the nitrate-deposited coatings more sensitive to substrate chemistry than the vacuum deposited coatings. This difference was particularly evident when nitrate coatings were sprayed onto the silver-coated barrier layers. Here, films could not be formed at all. The coatings coalesced into small islands, apparently the result of chemical attack of silver by nitric acid from the coating solution.

In some cases, the barrier layers could be used to enhance coatability. For example, the nitrate coatings did not adhere to unpolished polycrystalline Al_2O_3. With the addition of a $BaTiO_3$ barrier layer, however, adhering coatings could be formed. Hence, in addition to providing diffusion barriers, the sol-gel barrier layers can significantly affect coatability by changing the substrate chemistry and morphology, in both the positive and negative directions.

Substrate Diffusion

SEM micrographs of the Ta_2O_5 coating show a very smooth surface. Except for what seems to be cracking in the gold coating,

there is no apparent structure (porosity) in the film down to at least 300 Å. The RBS spectrum of a fired Ta_2O_5 coating shows a very sharp Ta peak, indicating that there is very little interdiffusion between the Ta_2O_5 and Al_2O_3 during the 950°C firing. Assuming the coating is dense, these RBS measurements correspond to a Ta_2O_5 coating thickness of about 600 Å. Auger sputter depth profiles of the same sample confirm the sharpness of the interface, but suggest a coating thickness of about 1550 Å, more than twice the RBS estimate. This discrepancy implies that, although coating shrinkage has long since stopped by 950°C, the Ta_2O_5 coating is not completely dense. For use as a barrier layer, this may have a significant, negative effect.

The RBS spectrum of the same Ta_2O_5 film after coating with the nitrate solution (1-2 μm) and firing shows an extension of the Ba peak, and especially of the Ta peak, indicating that interdiffusion between the superconductor and barrier coatings has taken place. The interdiffusion is more dramatically observed in an Auger sputter depth profile of the same sample. The barium has diffused into the substrate, leaving the bulk of the film deficient in Ba; the tantalum is evenly distributed throughout the bulk of the superconductor film; and, most importantly, the aluminum has diffused through almost the entire superconducting coating.

It is interesting that the sputter rate is significantly faster through the superconductor film than through the Ta_2O_5, suggesting that the mechanical integrity of the nitrate-sprayed superconductor coating on a Ta_2O_5 barrier layer is rather poor.

This is consistent with our observation of reduced adhesion for nitrate films on barrier layers.

X-ray diffraction patterns of fired nitrate coatings on bulk YSZ indicate that only the superconducting 1-2-3 phase is present. Diffraction patterns of a fired nitrate coating on a Ta_2O_5/sapphire substrate indicate the presence in addition to the 1-2-3 material, of impurity phases (Y_2BaCuO_5, $BaCuO_4$, and possibly others), as well as $BaCO_3$. The presence of phases other than the 1-2-3 is not surprising, in light of the extreme substrate/barrier layer/superconductor interdiffusion seen in the RBS and Auger results. The $BaCO_3$, however, is quite unexpected, since the barrier layers were fired to 950°C before coating with the nitrate solutions.

SEM micrographs of the YSZ coating show that the YSZ coatings are also smooth and featureless, at least down to the 300 Å level. When coated with the nitrate solutions and fired, however, the XRD pattern shows the presence of the same impurity phases, including $BaCO_3$ as in the Ta_2O_5 barrier layer. It is apparent that disruption of the 1:2:3 stoichiometry is just as severe with the YZS barrier coatings as with the Ta_2O_5 barrier coating.

This chemical interaction could be caused by incomplete densification before the nitrate coatings are applied, or by chemical attack of the superconductor during the rigorous heat-treatment to which the entire superconductor coating/barrier layer/substrate system was subject. Since YSZ is well established as one of the best (least reactive) substrates, it seems unlikely that the superconducting coating would severely attack these

coatings. Hence, there is strong indication that the YSZ coatings were not fully densified by the 900°C heat treatment, and that this relaxed porosity limits their effectiveness as barrier layers.

Resistivity vs. temperature measurements were made for all nitrate-coated and fired barrier layers. Since the thickness of the superconductor coatings can vary by multiple microns across a sample, however, it is difficult to quantify the effects of the different barrier layers. Qualitatively, minor improvements in electrical properties (such as a slight increase in onset temperature) have been observed when sapphire substrates are coated with these barrier coatings.