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## HIGH-TEMPERATURE CERAMIC SUPERCONDUCTORS

For Period  
May 24 - September 30, 1988

October 10, 1988

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GA Project 3850

Prepared by:

K. S. Mazdhyasni, Program Manager  
K. C. Chen, Project Engineer

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Approved by:



T. D. Gulden  
Director, Defense Materials

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1. INTRODUCTION

This is the first quarterly progress report on the work performed in the period from May 24, 1988 through September 30, 1988 on ONR Contract N00014-88-C-0714, entitled "High-Temperature Superconductors." The principal objectives of this program are (1) to demonstrate fabrication of high-temperature ceramic superconductors that can operate at or above 90 K with appropriate current density,  $J_c$ , in forms useful for application in resonant cavities, magnets, motors, sensors, computers, and other devices; and (2) to fabricate and demonstrate selected components made of these materials, including microwave cavities and magnetic shields.

The high-temperature ceramic superconductors system proposed was based on (1) the  $YBa_2Cu_3O_7$  ( $T_c \sim 95$  K) and its rare earth cogeners, which is the most studied material, and its chemistry is the least understood; (2) innovative processing technique, the alkoxides-based sol-gel process which is proven to be inherently suited to produce the high purity ceramic powder, fibers, and thin films required for viable devices to exploit this breakthrough in materials technology.

The sol-gel technique exhibits processing flexibility not available in traditional powder processing methods. Because of the high reactivity of the powder, one can achieve low processing temperatures which retain low boiling elements and enhance substrate compatibility. In addition to processing advantages, the sol-gel method achieves composition homogeneity and composition flexibility. Alkoxides mixed in the low viscosity liquid phase show a more complete and homogeneous mixing. Furthermore, we can add dopant more easily in the liquid phase, resulting in a composition tailored to the user need. The close control over purity and homogeneity afforded by sol-gel processing will allow control

of the characteristics of the grain boundaries which are likely to be central to the issue of maximizing the current-carrying capacity of the material.

The primary requirements for the sol-gel process are (1) the synthesis of suitable metal alkoxides of alkaline earth metals, yttrium and lanthanide elements and transition metals such as copper that are mutually soluble in a common organic solvent; (2) the hydrolysis of metal alkoxides and prevention of stable hydroxide formation; (3) the identification of an electrolyte and peptization of the resultant metal hydroxide to a sol; (4) gel formation; (5) the correlation of microstructure/processing/property relationships for the development of methods of synthesis and manufacture, leading to reproducible materials having the desired properties; and finally (6) process and input materials that are economically feasible.

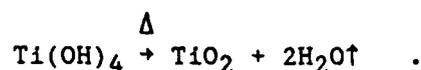
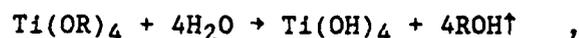
As mentioned before, many of the important applications of superconductors require material in the form of films. Detectors, magnetic cavities, and microcircuitry require superconducting material in the form of films. The sol-gel process is ideally suited to producing materials in these forms; in fact, it is used commercially to produce anti-reflection and mirror coatings.

Current polycrystalline high- $T_c$  superconducting (HTSC) monoliths have critical current density limits on the order of  $1000 \text{ A/cm}^2$ . However, current densities in the  $10^4$  and  $10^6 \text{ A/cm}^2$  range have been demonstrated in oriented polycrystalline films and single crystal films, respectively. The lower current densities are adequate for some applications such as in detectors and microwave cavities; however, many other applications require higher current densities. The single crystal data suggest that grain boundaries are the key to obtaining high current densities. A high degree of crystalline orientation (or texture) is probably required. Researchers at Arizona State University have shown, by transmission electron microscopy, the presence of a barium-rich amorphous phase at the grain boundaries in addition to a variety of other

planar defects. All of these are likely to influence the superconductivity properties.

Superconductors in the form of films are required for microwave and RF cavities, and could also be important as thin film tapes for applications in which wire might normally be used. Low loss and high gradients require the use of a Type-I materials, or development of strong pinning centers in the high- $T_c$  Type-II superconductors.

The dip coating technique has been successfully applied in the formation of sol-gel-based thin oxide films, of many compositions, on glass substrates. Some of these films are amorphous and some are polycrystalline. Earlier work is described by Schroeder (Ref. 1) and more recent work by Dislich and Hussman (Ref. 2). The overall chemistry is depicted by the simplified reaction for  $TiO_2$ :



The substrate is dipped into the sol-gel solution for a short time. After removal, the solvent is evaporated and hydrolysis and condensation follow. The film is then "hardened" by heat treatment at elevated temperatures. Since the density of the sol is usually not much greater than  $1 \text{ g/cm}^3$  and that of a polycrystalline oxide is greater than 2 or  $3 \text{ g/cm}^3$ , very large shrinkages must be anticipated, with nonuniform thickness and mechanical cracking of the film. However, with sufficient process control, high-quality films have been deposited on glass panes as large as  $3 \times 3 \text{ m}$  using this method (Ref. 2). A number of commercial products have been marketed by Schott of Germany, including sun shielding glass, mirrors, antireflection glasses, and fibers (Ref. 2). The absence of mechanical cracking when large contractions occur is truly remarkable. Apparently, the film shrinks predominantly in the thickness direction rather than in the lateral direction.

Some multicomponent oxide films are difficult to prepare by other methods, such as vacuum sputtering, because the deposition rates of the various species onto the substrate are difficult to control. Although recent results using physical vapor deposition (PVD) processes are encouraging, uniform distribution of dopant may also be a problem with PVD processes, as is the use of highly-complicated and costly vacuum equipment. The sol-gel method, on the other hand, does not require a sophisticated vacuum system; obtaining uniform distribution of various ions, including dopant, should pose no problem.

### 1.1. PROJECT OUTLINE

This program has been divided into six tasks: (1) metal alkoxide synthesis and processing, (2) microstructural evaluation and property measurement, (3) electrical and magnetic property measurement, (4) superconductor ceramic processing, (5) component fabrication and demonstration, and (6) reporting.

Task 1 is to synthesize a homogeneous alkoxides solution that contains all the constituent elements which can be easily made to powders, thin film, or drawn into fiber form. Ideally, this solution should possess precise stoichiometry, adequate stability, polymerizability, adherence, and spinnability. Also, the polymeric materials formed from this solution should be thermosetting, be able to be dissolved in organic solvents and contain as little as possible low-temperature pyrolyzable organics with high char yield.

Task 2 is to study the microstructure as a function of processing parameters. The study includes: density, pore size and pore size distribution, phase identification, chemical composition and purity, environmental stability, effects of heat treatment, residual strain, seeding, annealing in magnetic fields, and epitaxy on grain growth and orientation.

Task 3 is to study the electrical and magnetic properties of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (1, 2, 3) high  $T_c$  ceramic superconductors. It will include both the ac electrical resistance ( $R_{ac}$ ) and the ac magnetic susceptibility ( $\chi_{ac}$ ) magnetic properties.

The dc current versus voltage curve will be measured at liquid nitrogen temperatures for all promising superconducting materials and a value for  $J_c$  (77 K) determined. For the samples with the highest values of  $J_c$  (77 K), critical currents will be measured as a function of magnetic fields of up to 8 T at temperatures between 1.4 K and near the superconducting transition temperature  $T_c$ . These data will be collected in liquid He or flowing He using a Janis Superveritemp dewar equipped with an 8 T superconducting magnet. As required, Hall effect measurements can be performed in this apparatus to determine the type and density of the current carriers. Both  $\chi_{ac}$  and  $R_{ac}$  at pressures up to 20 kbar, can be used in this dewar to measure the superconducting and magnetic properties of samples at high pressures, at high magnetic fields and at temperatures from 1.4 to 300 K.

As a subcontractor to General Atomics (GA), Biomagnetic Technology Inc. (BTi), the world's leading company in the manufacture and use of a variety of SQUID systems, will support the basic materials characterization effort, as well as assist in prototype device fabrication. BTi will determine the diamagnetic properties of ceramics using a SQUID magnetometer to ascertain the approximate volume fraction of bulk superconducting material. Using other SQUID systems, BTi will perform measurements of the extremely weak magnetic and voltage signals expected in the measurement of superconducting, magnetic, and normal state electronic properties of films. BTi will also analyze and formulate requirements for the design of magnetic shields usable for both electronic and biomagnetic systems. BTi will also measure the quality of the superconducting film magnetic shields that GA will fabricate.

As a subcontractor to GA, the Superconductivity and Magnetism group under the direction of Professor M. Brian Maple, who is an international authority in superconductivity at the University of California, San Diego (UCSD), will be involved in the characterization of high-temperature superconducting oxide compounds, which are fabricated at GA. UCSD personnel will measure the superconducting and magnetic properties by means of measurements of the upper critical magnetic field, critical current density inferred from both direct and magnetization measurements, magnetic susceptibility, Meissner effect and specific heat. These laboratories are equipped to measure transport, thermal, superconducting, and magnetic properties as a function of temperature (50 mK to 300 K), magnetic field (to 10 T), and pressure (to 160 kbar). Both GA and UCSD personnel will collaborate on developing a low-temperature electron beam induced current (EBIC) capability using a scanning electron microscope to directly image superconducting current paths in these materials.

Figure 1 shows the detailed workscope for electromagnetic property measurements and microwave cavity testing and evaluation that GA and its subcontractors will perform.

Task 4 is an investigation of superconductor ceramic processing. Most of the important applications of superconductors require material in the form of fiber or films. Magnets, conductors, motors, and generators are examples of applications employing fiber; while detectors, microwave cavities, and microcircuitry require superconducting material in the form of films. The sol-gel process is ideally suited to producing materials in these forms; in fact, it is used commercially to produce antireflection and mirror coatings, and to produce continuous ceramic fibers, for structural reinforcement in composite materials, and for thermal insulation.

The brittleness of the oxide superconductors is a concern from the standpoint of fabricating and utilizing conventional wire. However,



beam theory indicates that the smaller the diameter of a "wire," the smaller the radius it can be bent to without exceeding the elastic limit. In fact, commercial sol-gel derived ceramic filament tows that can be woven into fabrics by conventional textile equipment are available from several sources. A further advantage of these filaments, which are 10 to 20  $\mu\text{m}$  in diameter, is that, as would be predicted from Weibull Theory, their strength is very high (in the 300 ksi range). This arises from the statistical nature of fracture of brittle materials which leads to a size dependence of fracture strength, with strength increasing dramatically as the thickness approaches the size of a critical flaw. Consequently, our concept of a superconducting "wire" is a conductor made up of multiple tows of fine, highly flexible filaments or fibers, perhaps imbedded in a good normal conductor like copper for protection in the event of local regions of superconductor going "normal."

The dip coating and/or rotating disc spin coating techniques will be applied in the formation of sol-gel-based thin films on a variety of ceramic substrates. Some of these films will be amorphous and some will be polycrystalline.

Thick films can be made by repeated dip-coating. Indeed, transparent noncrystalline silica slabs of several millimeters thickness have been made by many dippings of an inert substrate into sol-gel solution (Ref. 2). After densification these slabs are stable up to 1000°C. Alternate coating techniques such as plasma spraying and electrophoretic coating, should also be considered. In these cases sol-gel is the most controllable and flexible means of deriving the powders to be used in the coating process.

Based on results from Task 3, we will experimentally identify and define levels for the process parameters required to fabricate suitable simple geometry superconductor forms. The process parameters shall be systematically and iteratively investigated; specimens shall be prepared for several material/process combinations, and the effects of process

variations on properties shall be evaluated. Evaluation and characterization of specimens shall be conducted as in Tasks 2 and 3.

Fine fibers (8 to 20  $\mu\text{m}$ ) from the sol will be spun using a spinning machine (shown in Fig. 2) and subsequently gelled, cured, dried, and sintered to form continuous superconducting filaments that will be strong and flexible enough to form into conductors. Additionally, we will investigate the effect of certain superconducting perovskite oxide ceramic powder particles as seed material in order to crystallographically orient the fiber grains which exhibit high critical density,  $J_c$ .

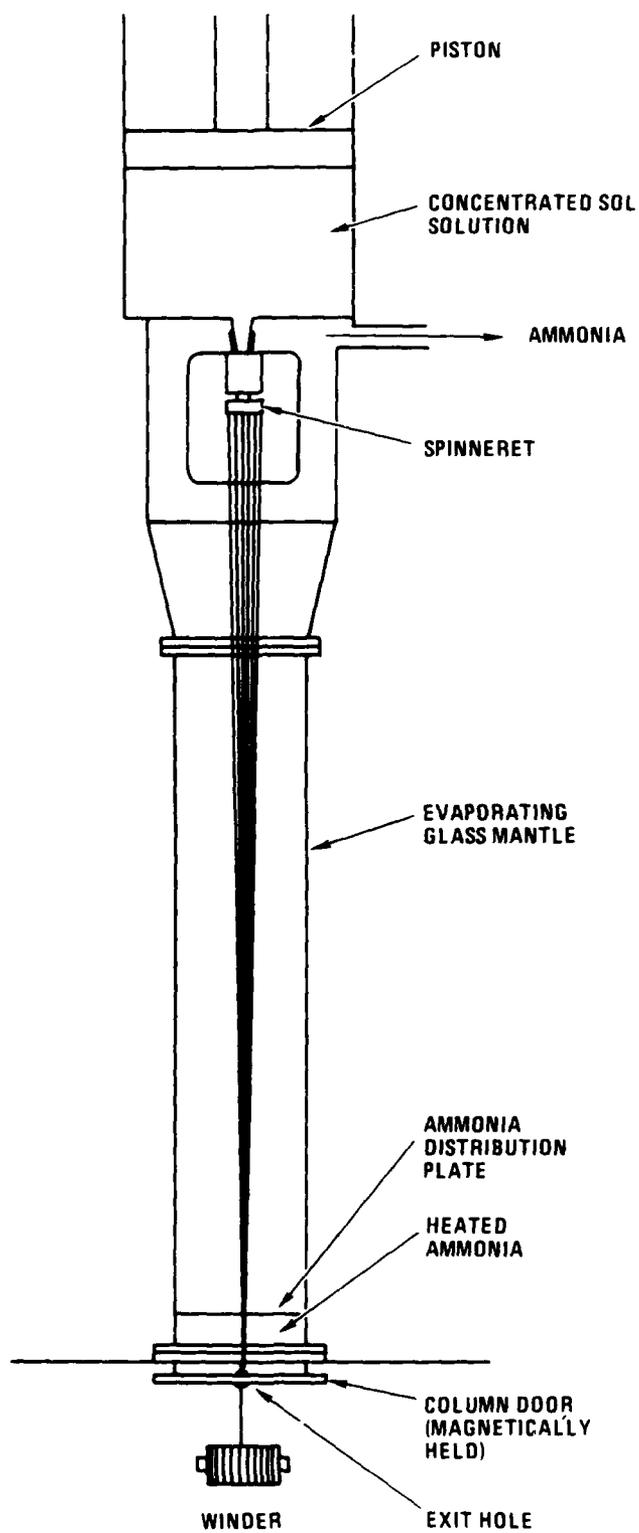
Various heat treatments will be evaluated to develop microstructures with maximum  $J_c$ . Particular attention will be devoted to determining how crystalline anisotropy is affected by processing and heat treatment.

Various heat treatments will be used to obtain a variety of grain sizes and preferred orientation. Thin film deposition and gelling of sols on fiber or wire substrates will also be examined. The possibility of epitaxy and of magnetic fields in controlling grain orientation will be investigated.

High density, fine grain size bodies will be fabricated by cold pressing and sintering and/or hot pressing under oxygen atmosphere. Attempts will be made to forge press the superconductor material for microstructural texturing in order to achieve high critical current density  $J_c$ .

Highly crystallized sol-gel-derived superconductor powders will be extruded or injection molded and densified in order to control grain orientation.

Thorough chemical, microstructural and electromagnetic property testing, as well as critical current density,  $J_c$ , property testing of



P-032(1)

Fig. 2. Fiber spinning apparatus

fabricated samples to determine compositional, structural, and processing variation among samples. Also, we will perform and document long-term stability tests in inert and ambient atmospheres.

A detailed chemical engineering analysis will be performed of the processes for formation of powders, fibers, and films with a strong emphasis on on-line process control. Optimized process flow sheets for large scale manufacturing will be developed.

Task 5 is to demonstrate component fabrication. GA will design and build a high Q, high  $T_c$  superconducting cavity using its unique sol-gel coating process capabilities. This task would proceed after some initial coating tests verified dc superconductivity and questions of adhesiveness, surface preparation, and processing procedures are answered. As the fabrication process and the materials quality are improved throughout the three-year program, two additional cavities will be constructed and tested. Coupling would be through a waveguide inductive iris into an end wall with a logarithmic decrement technique of Q measurement being considered most appropriate for the high Q anticipated. An X-band (10 GHz) frequency choice allows for convenient dimensions of 4.3 cm diameter by 2.8 cm height.

Another important application of superconductivity is in improving the Q of RLC tank circuits by greatly decreasing the resistance of discrete components. For example, this would allow much closer spacing of voice channels in shipboard high frequency (HF) communications. Currently, excessive RF resistive losses arise from current being confined to a 2 micron copper skin depth, resulting in Q factors of less than 1000 and requiring channel separations of nearly 1 MHz. GA proposes to coat conventional air-core inductor geometries and submit such samples to HF (10 MHz) tests of R/L times for varying choke geometries. (The superconducting penetration depth for all frequencies of interest is far less than any conceivable coating thickness.)

This study not only will establish the feasibility of high  $T_c$  superconducting technology applied to RF and microwave applications, but it also provides quantitative measurements and establishment of a technology database crucial to the successful fielding of future defense systems.

This report will focus mostly on the first task and briefly on Task 4.

## 2. PROGRESS

### 2.1 TASK 1 - METAL ALKOXIDE SYNTHESIS AND PROCESSING

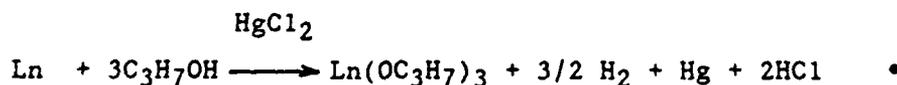
#### 2.1.1 Yttrium and Lanthanide Alkoxides

The electronegativity of yttrium and lanthanides places these elements between metals such as aluminum which forms covalent alkoxides and sodium which forms ionic alkoxides. The degree of ionic character of the M-O bond, which is dependent on the size and electronegativity of the metal atom, is important in determining the character of the alkoxide.

The study of alkoxides of yttrium and the lanthanides has been limited due to expensive starting materials and preparation and handling difficulties. Successful characterization of most of the alkoxides is complicated by their extreme sensitivity to moisture, heat, light, and atmospheric conditions.

#### 2.1.2 Synthesis

The yttrium and lanthanide tris-isopropoxides are prepared by the reaction of metal turnings with excess isopropyl alcohol and a small amount of  $\text{HgCl}_2$  ( $10^{-4}$  mol per mol of metal) as a catalyst (Ref. 3).

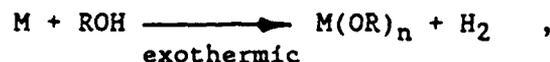


After filtration, the crude product is purified by recrystallization from hot isopropyl alcohol or vacuum sublimation. Yields of 75% or better are realized with this method. For some of the larger metal ions (lanthanum through neodymium), the reaction rate and percentage yield

are increased by using a mixture of  $\text{HgCl}_2$  and  $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$  or  $\text{HgI}_2$  (Ref. 3) for the catalyst.

Substitution of other R groups for the isopropoxy groups is accomplished by the alcohol interchange technique.

The alkaline earth metal alkoxides are prepared by the reaction of metal with alcohol. The reaction is highly exothermic with evolution of excess hydrogen.

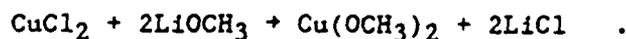


where M = the metal,

R = the isopropyl group

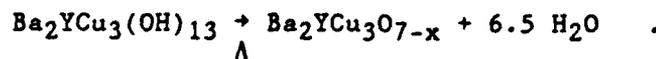
n = 1 or 2.

The copper methoxide and ethoxide are prepared by the reaction of anhydrous copper chloride/fluoride with lithium methoxide,  $\text{LiOCH}_3$  or lithium ethoxide,  $\text{LiOC}_2\text{H}_5$  in accordance with the following reaction:



## 2.2. HIGH $T_c$ CERAMIC SUPERCONDUCTOR POWDERS

The barium yttrium copper hydroxide,  $\text{Ba}_2\text{YCu}_3(\text{OH})_{13}$  was prepared by hydrolytic decomposition of their respective metal alkoxides. The hydroxide was then concentrated by evaporating the alcohol solvent and dried at  $110^\circ\text{C}$  for 1 to 2 h. The flow diagram is shown in Fig. 3.



At this stage the hydrated hydroxides consist of finely divided particles. The as-prepared powder showed a mixture of various yttrium barium

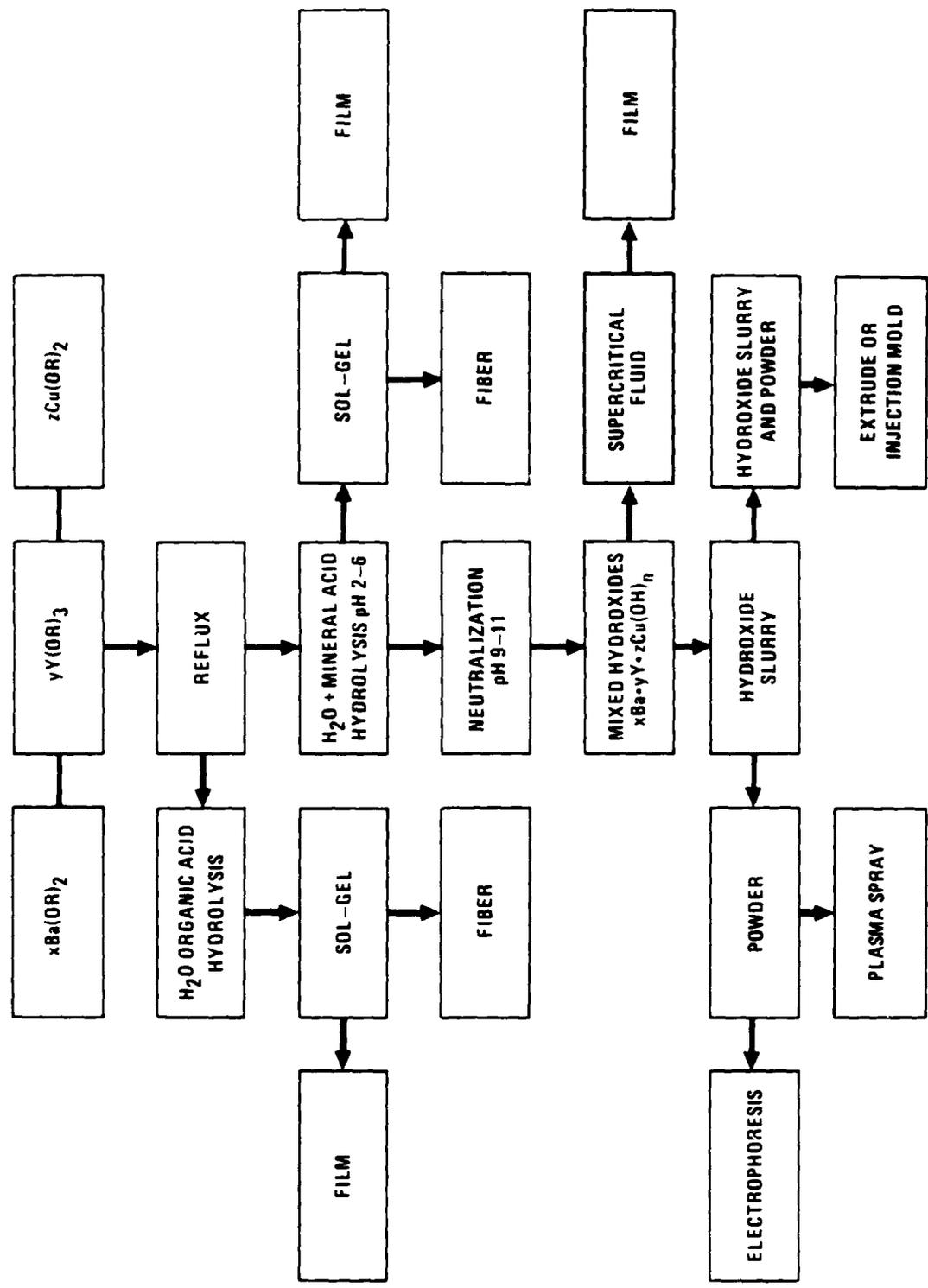


Fig. 3. Flow diagram for BaYCuO high-temperature superconductor precursor preparation

P-060(3)

cuprates when examined by X-ray diffraction. Emission spectrographic analysis of the powder after it was calcined at 675 deg for 1 h is shown in Table 1. The table lists results obtained from two batches of sol-gel precursor subsequently converted to oxide. Separate analyses for the oxide demonstrated the maintenance of high purity levels on a continual basis. The wet chemical analyses performed on the same sample powder indicated Y/Ba/Cu ratios of  $1/2/3 \pm 0.06$  which is within the experimental error.

### 2.3. THERMOGRAVIMETRIC ANALYSIS OF THE AS-PREPARED POWDER

The thermogravimetric analysis (TGA) of the as-prepared and dried at 110°C powder sample in air is shown in Fig. 4. The 15% to 18% weight loss in the temperature range of 180° to 230°C, with the maximum rate at 230°C, is attributed to the decomposition of copper precursor to copper oxide. The 5% to 8% weight loss in the temperature range of 300° to 500°C with a maximum rate of 420°C is due to the dehydration of  $Y(OH)_3$  to  $Y_2O_3$  and combustible organic residue from the parent alcohol. Finally, the 15% to 18% weight loss occurring within a relatively narrow temperature range 575° to 690°C is thought to be associated with the  $Ba(OH)_2$  decomposition to BaO. Although not shown in Fig. 4, additional weight loss up to 2% was recorded on grinding of the powder material and calcining in the temperature range of 700° to 750°C. This weight loss is not observed in subsequent heat treatment and is attributed to residual carbon which may have been trapped in the material during initial TGA studies.

### 2.4. CALCINATION IN VARYING ATMOSPHERE

Calcination was studied to observe the solid state reaction of cuprate to crystalline high  $T_c$  superconductor powder in air and oxygen atmosphere.

The powder sample was heat treated in yttria stabilized zirconia and/or alumina crucibles in both air and oxygen in the temperature range

TABLE 1  
EMISSION SPECTROGRAPHIC  
ANALYSIS Y-Ba-Cu  
OXIDE

Element	PPm
Al	N < 50
Ba	Major
Be	N < 10
Bi	N < 50
B	N < 10
Cd	N < 10
Ca	N < 500
Cr	N < 50
Co	N < 10
Cu	Major
Ge	N < 50
Au	N < 10
Hf	N < 500
Y	Major
Fe	N < 10
Pb	N < 10
Li	N < 10
Mg	N < 10
Mn	N < 10
Mo	N < 10
Nb	N < 10
Ni	N < 10
P	N < 500
Si	300
Na	N < 500
Sr	N < 500
Zn	N < 100
Zr	N < 50

N < means less  
than not detected.

# TGA

Size: 14.0030 mg  
Method: INORGANIC TGA  
Comment: 5.00 °C/MIN O2 ATMS.  
120

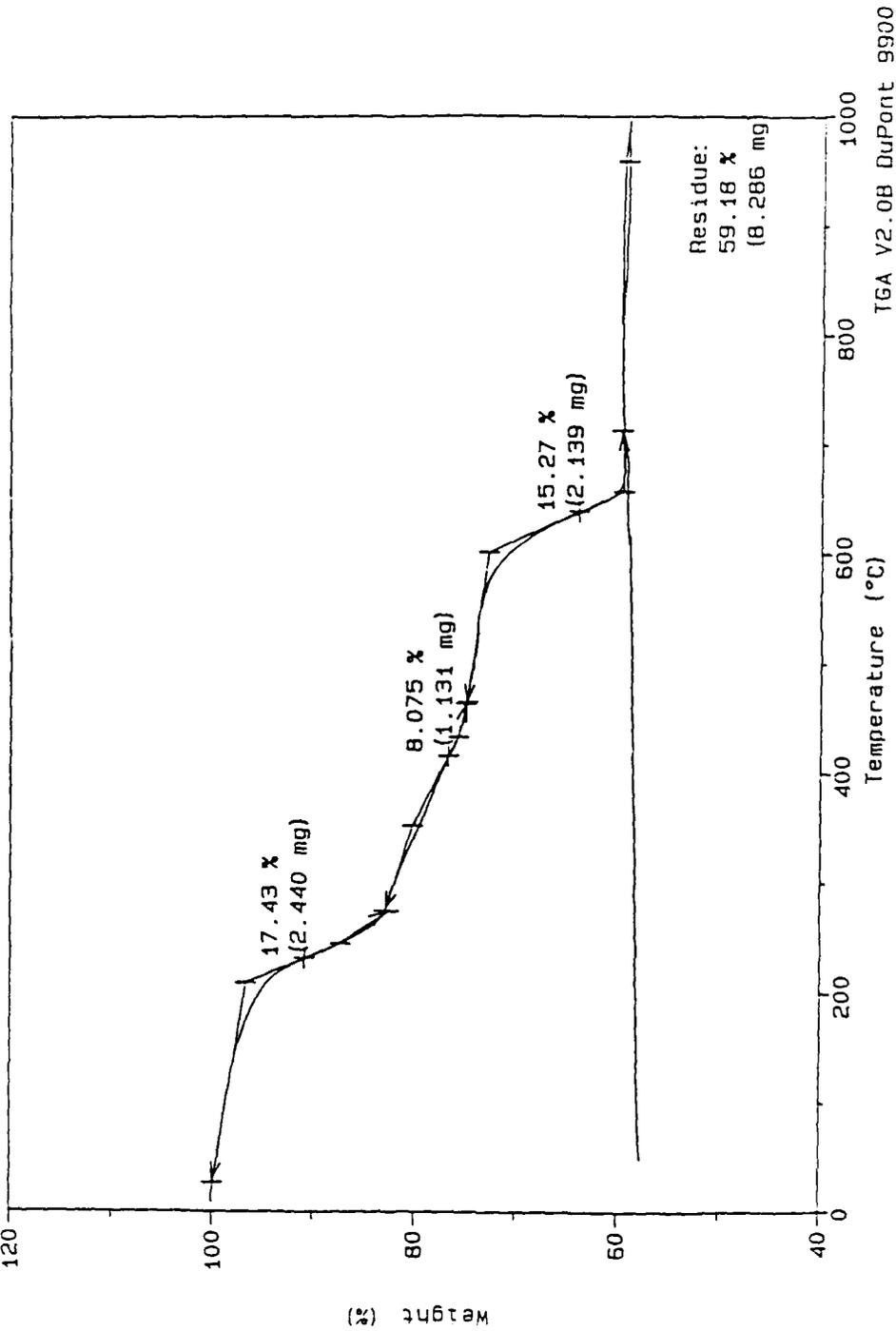


Fig. 4. TGA of sol-gel derived  $YBa_2Cu_3O_{7-x}$

of 300° to 950°C and then X-rayed at room temperature. Up to 700°C, the mixed cuprate state was retained, and from 750° to 800°C there was predominantly single phase orthorhombic yttrium barium cuprate (1, 2, 3) solid solution plus a few very small intensity unidentified peaks were observed. The X-ray diffraction powder patterns obtained using CuK $\alpha$  radiation indicate that a transformation to orthorhombic phase overlapping the cuprate phase occurred at 750°C. However, no further change in the crystal structure occurred after prolonged, up to 60 h, heat treatment of the powder at 750°C in either air or oxygen atmosphere. This suggests that perhaps transformation in this system is a bulk phenomenon and is not a function of nucleation and growth of a fine particulate to a larger crystallite size superconductor oxide powder.

#### 2.5. FABRICATION AND SINTERING OF HIGH T<sub>c</sub> SUPERCONDUCTOR

Based on the TGA study, the sol-gel derived powders were calcined at 700°C for 30 min and then ground in a B<sub>4</sub>C mortar to effect comminution of the larger agglomerates. The very fine highly active black powder was again heat treated to 700°C for another 30 min in order to assure removal of all volatile species. Due to the moisture sensitivity and reactivity of high T<sub>c</sub> superconductor material with CO<sub>2</sub>, excessive exposure of the powder material to an ambient atmosphere was avoided by working in an inert atmosphere dry box.

Specimens 1-1/4 and 1/2 in. in diameter and 1/8 in. thick were uniaxially cold pressed in a steel die at 15 to 80 Kpsi. The compacted bodies were placed on their edge on a bed of the same powder in a shallow alumina boat and sintered in O<sub>2</sub> (approximately 60 cc/min oxygen flow rate) at a maximum temperature of 950°C. The sintering schedule used was as follows: 60 min ramp up from room temperature of 900°C immediately followed by a 30 min ramp up to 950°C and soak time of 12 to 16 h. The furnace was cooled down at a rate of 1°C/min to 450°C and held at 450°C for 12 h and then was allowed to cooldown to room temperature. The sintered bodies approached near theoretical density (6.4 g/cm<sup>3</sup>) for orthorhombic high T<sub>c</sub> superconductor). For very dense bodies much longer

anneals in O<sub>2</sub> at higher temperatures, 680°C, was required to obtain fully orthorhombic phase. Figure 5 shows a powder X-ray diffraction pattern of a typical sintered body.

## 2.6. RESISTIVITY AND MEISSNER EFFECT

Figure 6 shows a resistance curve versus temperature of the pure YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> high T<sub>c</sub> superconductor ceramic materials. An expanded resistance curve for the resulting material, showing a sharp (1 to 2 K) superconducting transition just above 90 K. Samples prepared exhibit superconductivity by the levitation screening technique (see Fig. 7).

The preliminary results indicate that high purity sol-gel derived high T<sub>c</sub> superconductor ceramic with very sharp transition temperatures (1 to 2 K), is readily made.

## 2.7. FIBERS AND FILMS

Yttrium and barium isopropoxides solutions can be easily prepared and pose no problem in the final solution preparation. However, the copper methoxide and ethoxide have low solubilities in ethanol and propanol. Since it has been reported that the solubility of the alkoxides can be greatly increased by formation of a double alkoxide with some elements, the study was focused on the preparation of double alkoxides of barium-copper, yttrium-copper double alkoxides.

The double alkoxide of yttrium-copper was prepared by first dissolving anhydrous copper chloride (or fluoride) and yttrium chloride (or yttrium isopropoxide) in dried isopropanol and then reacting with lithium or sodium isopropoxides. It was found that the rate of dropwise adding the lithium (or sodium) isopropoxide and the temperature of the reaction are critical. The slower the rate of addition, the coarser the lithium (or sodium) chlorides precipitates. This coarse precipitate facilitates the separation of the precipitates from the solution. The

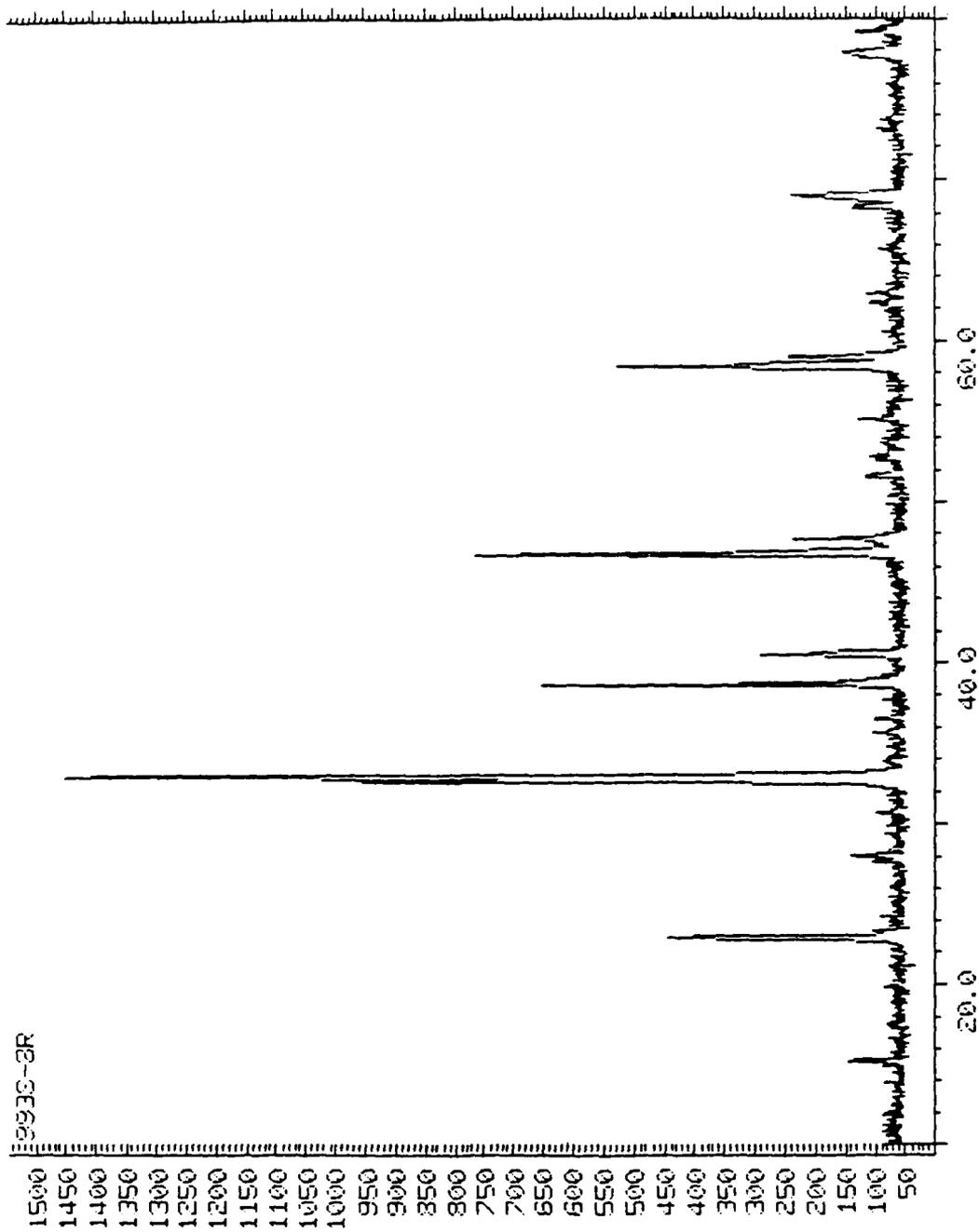
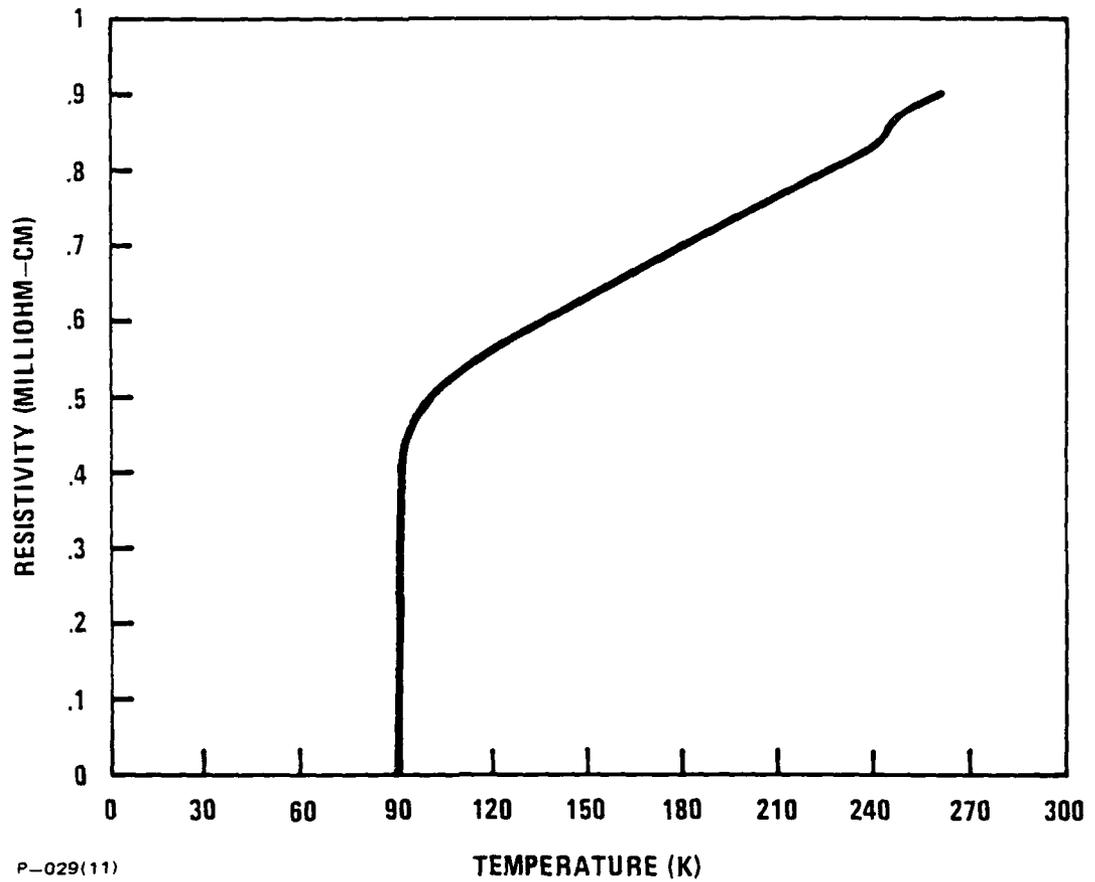
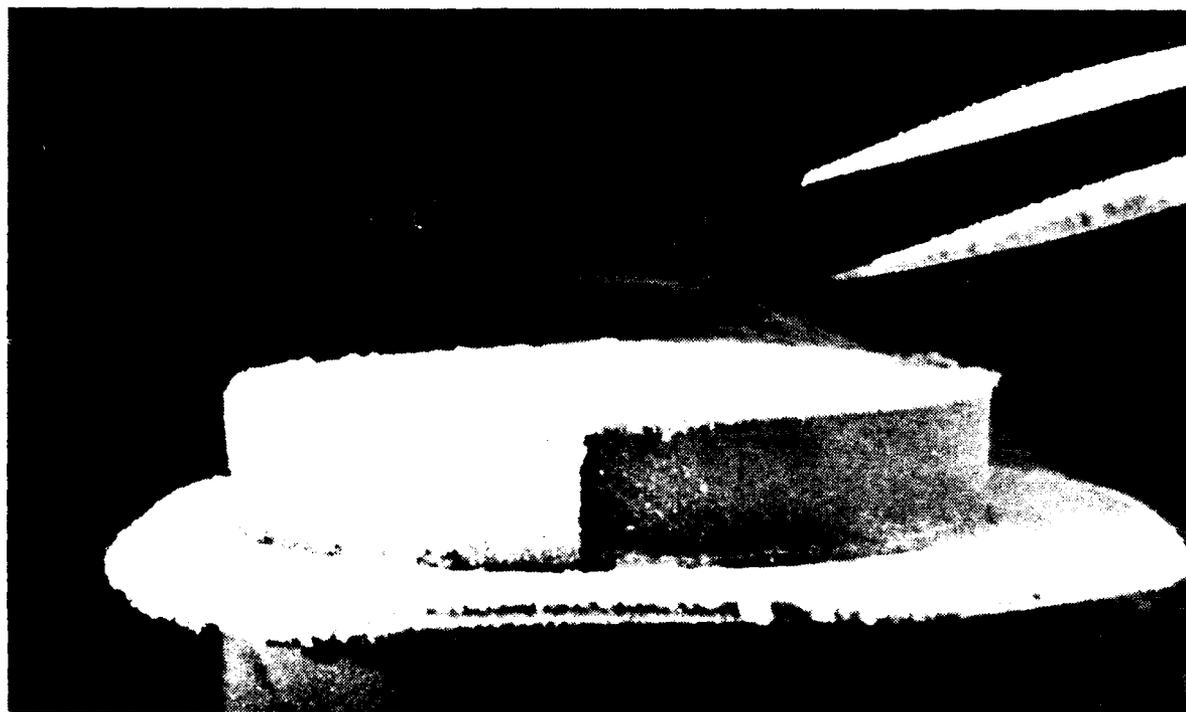


Fig. 5. X-ray diffraction pattern of fully crystalline orthorhombic sol-gel derived  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$



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Fig. 6. Resistance curve for sol-gel-derived  $\text{YBa}_2\text{Cu}_3\text{O}_7$  showing superconducting transition at 90 K. Note also the small drop in resistance at 240 K.



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Fig. 7. Sol-gel-derived high-temperature superconductor levitated on neodymium-iron-boron magnet at 77 K

solution does contain appreciate amount of copper. In the beginning of the lithium (or sodium) addition, the precipitates appear to be white. When more than half of the required amount of lithium (or sodium) was added, the precipitates became greenish. This green color indicated incomplete reaction of copper chloride. The chemical analysis by X-ray fluorescence spectrometry indicates not only the loss of copper but also some contaminations of lithium (or sodium) and chlorine. It is suspected that the copper may exist in the form of a copper alkoxide-chloride.

Barium isopropoxide was used in place of the sodium isopropoxide in the barium-copper double alkoxide preparation to reduce the contamination of the sodium in the solution. Copper methoxide has been reacted with lithium isopropoxide and then further adding barium isopropoxide to see if the double alkoxide could be made. Several reaction sequences and different solvents, such as benzene, have been tried. But in all events, loss of the copper persisted, as described above.

In view of the above observation, the double alkoxide route was temporarily abandoned. The investigation was carried out to find out the use of copper salts for solution preparation. Anhydrous copper acetate was found to dissolve only 0.3 to 0.5 g per 100 ml of dried isopropanol. Even in boiling isopropanol, it also dissolves less than 1 g per 100 ml of isopropanol. The copper ethylhexanote  $[\text{Cu}(\text{O}_2\text{C}_8\text{H}_{15})_2]$  was found to be very soluble in *i*-propanol. It will be used for latter solution preparation.

#### 2.8. SUBTASK 2 - CONTROL OF THE NUMBER OF ACTIVE FUNCTIONAL GROUP IN ALKOXIDES

To form a useful ceramic fiber from sol-gel, all the parameters shown in Fig. 8 must be understood and reproducibly controlled. In order to acquire suitable properties (namely, adequate solution stability, high solubility in organic solvents, spinnability, and thermosetting properties) in the polymeric material for fiber drawing, the structure of the solutions should first be controlled.

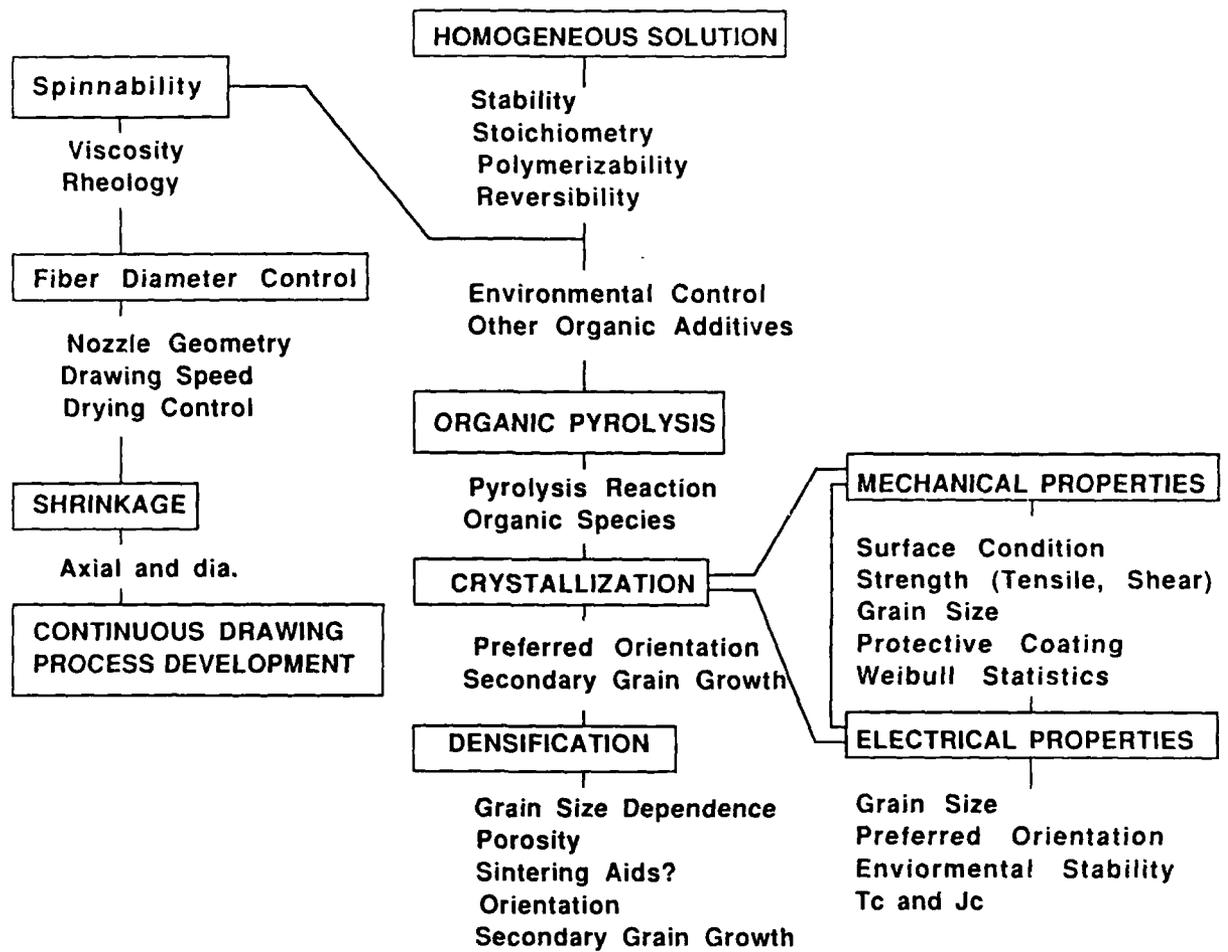


Fig. 8. Fiber process parameters

It is known that if each monomer contains more than three functional groups, a three-dimensional rigid network will form upon complete polymerization. Therefore, the number of active functional groups per molecule should be limited to two (or close to two) for the polymer to have some degree of flexibility. The two-dimensional chain-type structure should provide spinnability for fiber drawing and, at some time, have a better chance to be dissolved in organic solvents. To achieve this requirement in alkoxides, the alkoxy group can be replaced by organic acids or beta-diketones. Since molecular structures of the alkoxides are not clear at the present time, the exact amount of organic acids needed to achieve chain-type structure should be determined experimentally.

Yttrium and barium isopropoxides were mixed in one to two molar ratio and were refluxed to obtain a possible "double alkoxide." An organic acid, e.g., 2-ethylhexanoic acid, was added to this solution in different molar ratios to replace the active alkoxy groups. The molar ratios of 2-ethylhexanoic acid added were 5.17/1, 2.67/1, 2.05/1, 1.5/1, and 1.0/1 of the total molar alkoxides in the solutions. The resultant solutions were exposed to moisture and concentrated to see if they would become viscous liquids. The fiber forming properties of those viscous polymeric materials were examined. After evaporation of solvents, the solutions with greater than 1.5/1 molar ratios of the acid became viscous. They can be successfully hand-drawn into fiber.

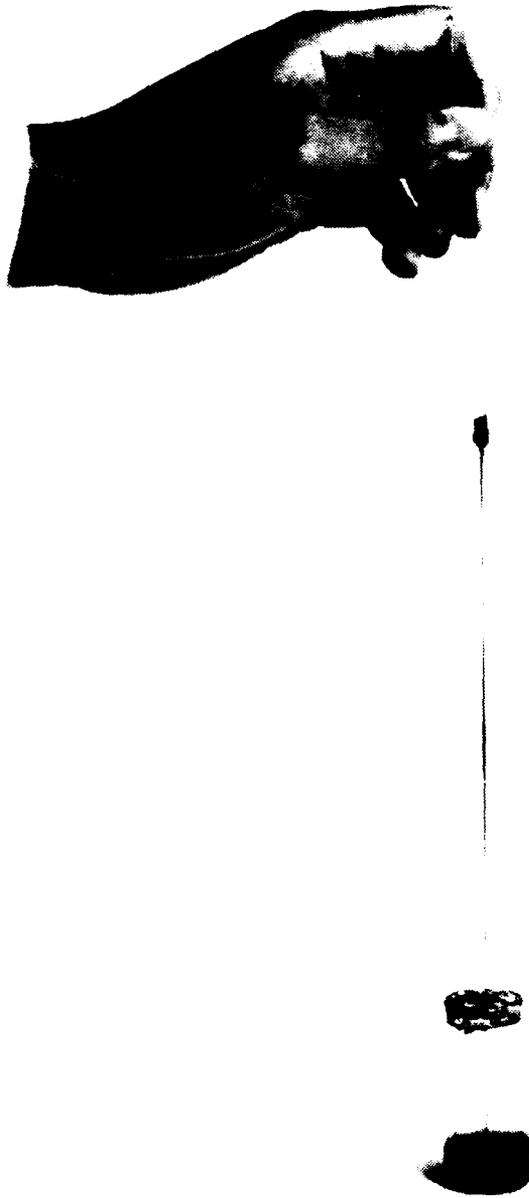
The attached organic acid groups, however, can not be removed by low temperature evaporation. They have to be removed by high temperature pyrolysis. Therefore, the optimal condition will be to maintain the viscous state but reduce the amount of residual organics as much as possible. Reduction of the amount of organic acid in the polymeric materials also have the advantage of smaller shrinkage and less chance of forming barium carbonate during firing. At the present time, the solution with 1.5/1 molar ratio acid addition seems to best fit all

these requirements. A short fiber has been successfully drawn from this solution, and retains its fiber form even after 900°C heat-treatment.

### 2.9. SUBTASK 3 - PREPARATION OF SOLUTION CONTAINING THREE NECESSARY ELEMENTS WITH FIBER FORMING ABILITIES

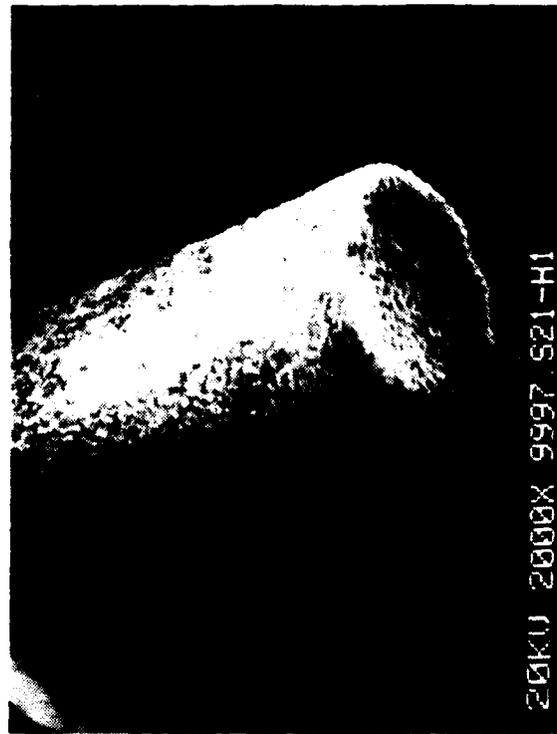
From Subtask 1, copper ethylhexanoate was found to be suitable for homogeneous solution preparation. After mixing yttrium and barium alkoxides in 1:2 ratio, a equivalent amount of 1.5/1 molar ratio of 2-ethylhexanoic acid/alkoxides was introduced to modify the structure of this alkoxide(s). To this homogeneous solution, copper ethylhexanoate propanolic solution was added. The volume of the solution was around 400 to 500 ml. By refluxing this solution in nitrogen atmosphere for 30 to 60 min, a greenish precipitate was formed. When a few milliliter of water-propanol solution was distilled into the solution, the greenish precipitate immediately dissolved and a dark brownish green solution formed. This solution was further concentrated till the volume of the solution was around 50 ml. A dark greenish brown precipitate formed on the bottom. The solution was distilled until almost dry. This precipitate was found to completely dissolve in less than 5 ml of benzene. The solution was a clear dark brown solution. This dark brown solution was further concentrated to 0.5 to 1 ml. At this point, the solution became highly viscous and could be easily hand-drawn into fibers (see Fig. 9). Fibers as long as 80 cm can be easily drawn. The fibers have adequate mechanical strength right after drawing and are flexible. They retained strengths and flexibility for about 5 days. After 5 days in ambient atmosphere, the fibers became more brittle. Short fibers have been heat treated up to 900°C for 5 h. Further study has to be done on the refinement of the heat treatment schedule (see Fig. 10).

Even though the solution possessed good fiberizability, it was not at the right stoichiometry. Due to the small amount of the sample prepared for the fiberizability test, small errors in the alkoxide solution concentrations and volume measurements can create a large drift in the composition from the intended (1,2,3) composition. Further experiments



1-784(2)

Fig. 9. Sol-gel derived preceramic superconductor fiber



1-784(1)

Fig. 10. SEM micrographs of sol-gel derived ceramic superconductor fibers (900°C, 5 h)

are being carried out to calibrate the solution concentrations to determine if the drift from the intended composition was due to the errors in the starting composition of the solution or due to loss of some element during pyrolysis.

#### 2.10. SUBTASK 4 - CALIBRATION OF SOLUTION CONCENTRATIONS

From Subtask 3, it is obvious that an accurate control method for determination of the solution concentrations is necessary. A method which is accurate, rapid, and adaptable for control purposes is titrimetry. The following paragraphs describe the standard titration procedures used for the determination of the concentrations of the solutions. These procedures have to be modified to remove i-propanol and other organic species and to adjust the solution pH before the standard procedure could be used.

##### 2.10.1. Determination of the Concentration of Yttrium Alkoxide Solution

EDTA titration is suitable for determination of rare earths (Ref. 5). To the slightly acidic solution, add a few crystals of NaK-tartrate, 5 ml pH 10 buffer per 50 ml of the solution until the pH of the solution is 8-9, and eriochrome black T indicator, and titrate the boiling solution with 0.1 M EDTA until the color becomes blue.

##### 2.10.2. Determination of the Concentration of Barium Alkoxide Solution

To the barium aqueous solutions, add two drops of acetic acid, boil for 5 min, cool, add 10 ml buffer (8.25 g  $\text{NH}_4\text{Cl}$  and 113 ml  $\text{NH}_4\text{OH}$  diluted to 1 liter), and 0.4 g indicator (0.25 g eriochrome black T in 25 g  $\text{NaCl}$ ) and titrate with EDTA reagent solution. For the EDTA reagent solution, dissolve 2.6 g  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 1.9 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 28.0 g EDTA and 7.9 ml 50%  $\text{NaOH}$  in  $\text{H}_2\text{O}$  and dilute to 1 liter. Titrate with EDTA until the color changes from wine-red to blue.

2.10.3. Determination of the Concentration of Copper Ethylhexanoate Solution

Method 1 (Ref. 4). Dilute 25.0 ml of the copper solution (0.02 M) to about 100 ml with distilled water and add to the weakly acidic solution sufficient pyridine to produce an intense blue coloration. Add five to six drops of pyrocatechol violet as indicator and titrate with standard EDTA until the solution acquires a yellowish-green (or green) color.

Method 2. For <20 mg in 100 ml acidic solution, add 0.5 g  $\text{NH}_4\text{NO}_3$ , four to five drops 0.1% pyrocatechol violet indicator and 0.5 N  $\text{NH}_4\text{OH}$  to give a blue color; add 1 to 2 g  $\text{NH}_4\text{OAc}$  and titrate with 0.02 to 0.1 M EDTA to a yellow color (Ref. 5).

At the present time, the concentrations determined by these method are within 0.5% to 1% error. Further refinements of these procedure are in progress to reduce this error. Solutions containing all three elements are being prepared using these calibrated solutions.

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