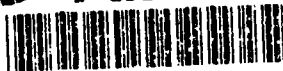


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PROCESSING AND FABRICATION OF HIGH TEMPERATURE OXIDE SUPERCONDUCTORS

By: Sylvia M. Johnson and Michael I. Gusman

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13. ABSTRACT (Maximum 200 words) Synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductor powders by freeze-drying was developed. The freeze-drying process consists of forming a solution of Y and Cu nitrates and Ba acetate, freezing, sublimating the water and calcination. The effect of processing variables on the powder characteristics, including surface area, size, stoichiometry, agglomeration, were investigated. Stoichiometry control requires control of the chemistry of the system, and careful analysis of starting solutions is required to prepare powders of the desired composition. Powders were sintered into pellets and the superconducting behavior was evaluated. Stanford University served as a subcontractor and was responsible for most of the critical transition temperature and critical current measurements.					
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A major result of this work was the development of an improved calcination technique which can be used to produce superconductor and other powders which are free of contamination by carbonates, especially BaCO_3 . The calcination process consists of two stages, a low temperature treatment in a fluidized bed in NO_2 followed by a higher temperature calcination in O_2 . In the first step, the acetate anion is removed and replaced with nitrate. BaO is thus prevented from forming BaCO_3 reacting with CO_2 formed on decomposition of acetate. The nitrates are decomposed in the second step and the oxides react to form the superconductor. A patent was obtained on the calcination procedure.

Materials fabricated from powders calcined by the improved technique show an improvement in critical current density by a factor of 2. The highest J_c was $14,400 \text{ A/cm}^2$ at 5K and 0.5T. However, this J_c was obtained on a non-optimized sample, and considerable improvements are possible.

Freeze-drying was shown to be a relatively simple method for synthesizing high purity, homogeneous superconductor powders. Scale-up of the method should be relatively straightforward. Understanding and control of the chemistry at all stages of synthesis and processing are required to produce high quality powders.

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SUMMARY

Recently discovered high temperature superconductors are ceramics, and, in common with other ceramics, the quality of the new superconductors depends on the characteristics of the starting materials and on the processing route.

The objective of this program was to investigate and develop a synthesis technique for powders of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and to process these powders into ceramic monoliths. A freeze-drying technique was developed at SRI International for synthesizing the powders. Stanford University was a subcontractor and was responsible for evaluation of superconducting properties such as critical temperature and critical current density.

Freeze-drying consists of preparing a solution containing the desired cations, spraying the solution into a cryogenic fluid, (usually liquid nitrogen), placing the frozen material into a freeze-dryer and subliming the water, and calcining the dried material to remove volatiles and react the oxides.

Freeze-drying produces high purity, homogeneous, high surface area and active powders, they may be easily doped. The process is also amenable to scale-up and potentially inexpensive. However, it is necessary to control the chemistry at all points in the process.

Results of this program include identification of the important processing variables and a process for producing high quality powders. Stoichiometry control was found to be a problem, but it was solved by careful analysis of the starting materials and careful selection of starting materials. Other variables of interest are the pH of the solution, the concentration, and the spraying technique.

To maximize yield it was found necessary to use Y nitrate, Cu nitrate, and Ba-acetate. An all nitrate solution cannot be used except at very low concentrations because of the common anion effect. However, the use of acetate/nitrate mixtures presents two problems. First, care must be taken on heating because such mixtures are explosive. Second, the acetate can decompose and react with BaO to form BaCO_3 , which is deleterious to the superconducting properties.

The early powders were made using the standard technique of calcining the powders in a crucible. However, as larger quantities of powder were prepared, BaCO_3 contamination became serious and new calcination process had to be developed.

The development of an improved calcination technique for producing carbonate-free superconductor and other powders was a major result of this work. The calcination process consists of two stages: a low temperature treatment in a fluidized bed in NO_2 followed by a higher temperature calcination in O_2 . In the first step, the acetate anion is removed and replaced with nitrate. BaO is thus prevented from forming BaCO_3 by reacting with CO_2 formed on decomposition of acetate. The nitrates are decomposed in the second step and the oxides react to form the superconductor. A patent was obtained on the calcination procedure.

Powders were compacted and sintered by various routes and superconducting properties characterized. Materials fabricated from powders calcined by the improved technique show an improvement in critical current density by a factor of 2. The highest J_c was $14,400 \text{ A/cm}^2$ at 5K and 0.5T. However, this J_c was obtained on a non-optimized sample, and considerable improvements are possible.

In summary, at the end of this program, a process for producing powders of $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ was developed. This process was based on freeze-drying. A calcination procedure applicable to freeze-dried and other precursors was also developed and patented.

Further work in this area should be addressed towards refining the calcination process and engineering the process to be continuous. Further sintering studies and superconducting characterization is required. However, the freeze-drying process has been shown to be an efficient technique for producing high quality carbonate free superconductor powders.

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1. INTRODUCTION

The discovery of high temperature oxide superconductors by Bednorz and Muller¹ and the later discovery of compounds with higher critical temperatures, including the Y-Ba-Cu-O (YBCO) family,² the Bi-(Pb)-Sr-Ca-Cu-O (BSCCO) family,³ and the Tl-Sr-Ca-Cu-O materials,⁴ have stimulated considerable efforts to prepare these materials as powders and to process them to form films, coatings, and bulk materials. The success of high temperature superconductors in a wide variety of defense applications requires that materials synthesis and processing be understood so that high quality reliable components can be fabricated.

The high critical current densities and sharp and complete transitions from the normal to the superconducting state in copper-based superconductors, requires that all steps in the processing and handling of these materials must be controlled to ensure that materials of the desired stoichiometry, phase composition, purity, and microstructure are produced. Particularly important in bulk materials are grain boundary characteristics, grain shape and alignment, and the phase composition. In common with other ceramic materials, these features have their roots in the characteristics of the starting powders and the processing techniques used to form bulk materials.

The preparation of high quality superconductors therefore requires techniques for controlled synthesis of powders. Ideally, powder synthesis techniques should be readily adaptable to the synthesis of powders of different composition (important in the area of superconductivity where new materials are being developed rapidly); should be simple and scalable so that large quantities can be prepared at reasonable cost; and should produce powders that can be easily formed into bulk materials. Powders should be of high purity, controlled particle size, and controlled stoichiometry.

Techniques for preparing powders include grind/calcining, coprecipitation,⁵ various aerosol techniques,⁶ sol-gel, and freeze-drying.^{7,8} Freeze-drying is attractive because it is easily scalable, and it produces very homogeneous, high purity powders. Freeze-drying for the synthesis of superconductor powders was developed at SRI International.⁹ In brief, freeze-drying consists of preparing solutions of soluble salts of the desired cations, spraying this solution into a cryogenic fluid to freeze the droplets, subliming water in a freeze-dryer, and calcining to remove volatiles and form the desired phase, followed by further processing as appropriate.

This report describes the results of a study performed by SRI to investigate synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders by freeze-drying and then processing and evaluating the powders and materials. The objective of the work was to develop an understanding of the synthesis technique and thus improve the powders to result in materials with improved superconducting properties. Only powders in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ system were studied. We have made significant advances in understanding the synthesis technique. The most important result of this work was the development of a new approach to calcination, which resulted in the production of carbonate-free powders and a doubling, at least, in the critical current density. The original process was patented during the project, and a U.S. patent for the improved calcination process has been granted.

Stanford University was a subcontractor in this effort and was responsible for superconducting measurements. Stanford University also prepared some films from targets prepared by SRI from the powder obtained by freeze drying.

This report describes the techniques used and the results obtained in the program. The important development made in obtaining carbonate-free powders is summarized separately in Section 5.

2. SYNTHESIS AND PROCESSING

MATERIALS AND EQUIPMENT

The purities and sources of the chemicals used in this study are given in Table 1. The equipment used at SRI is listed in Table 2.

Table 1

Purities And Sources Of Chemicals

<u>Chemical</u>	<u>Purity/Size</u>	<u>Supplier</u>
Y(NO ₃) ₃ ·6H ₂ O	99.9%	Johnson-Matthey
Ba(C ₂ H ₃ O ₂) ₂	ACS	Johnson-Matthey
Cu(NO ₃) ₂ ·6H ₂ O	99.999%	Johnson-Matthey
Cu	OFHC	Anaconda
O ₂	99.6%	Liquid Carbonic
Yb(NO ₃) ₃	99.9%	Johnson-Matthey
EDTA	0.0997 M	Aldrich

Table 2

Equipment Sources

<u>Equipment</u>	<u>Manufacturer</u>
Freeze-dryer (2-tray)	FTS
Freeze-dryer (4-tray)	Virtis
Ultrasonic nozzle	Sonotek
Peristaltic pump	Cole-Palmer
2-in.-diameter elevator furnace	Keithley
12 x12 x 12 in. elevator furnace	C & M Furnaces
Large muffle furnace	Thermolyne
2-in.-diameter quartz tube furnace	C & M Furnace
820 Cryogenic thermometer	Lake Shore Cryotronics
181 Nanovoltmeter	Keithley
224 Programmable current source	Keithley

POWDER PREPARATION BY FREEZE-DRYING

General techniques for powder synthesis and processing are described below as well as approaches to modifying these techniques. Some modifications to the powder synthesis technique are discussed in more detail in Section 4. In addition, significant changes to the calcination procedure are described in Section 5.

The freeze-drying process for producing oxide powders consists of four basic steps: solution preparation, spraying, freeze-drying, and calcination. Each of these steps and improvements in the techniques developed during the program are described separately below. A flow chart of the powder preparation method is shown in Figure 1. Specific procedures for preparing $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) are given in Table 3.

Table 3

Preparation of YBCO By Freeze-Drying

Solution Preparation

Cu nitrate: Dissolve high purity Cu in HNO_3 .

Y nitrate: Dissolve $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in distilled water. Analyze solutions for Y content.

Mix Cu nitrate and Y nitrate solutions together at $\sim 50^\circ\text{C}$.

Ba acetate: Add $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ to nitrate solution immediately before spraying.

Concentration: $\sim 0.13 \text{ M}$ (in YBCO).

Adjust pH to ~ 4 with NH_4OH .

Spraying

Spray solution through an ultrasonic sprayer at $\sim 4 \text{ L/hr}$ into LN in stainless steel trays.

Freeze-Drying

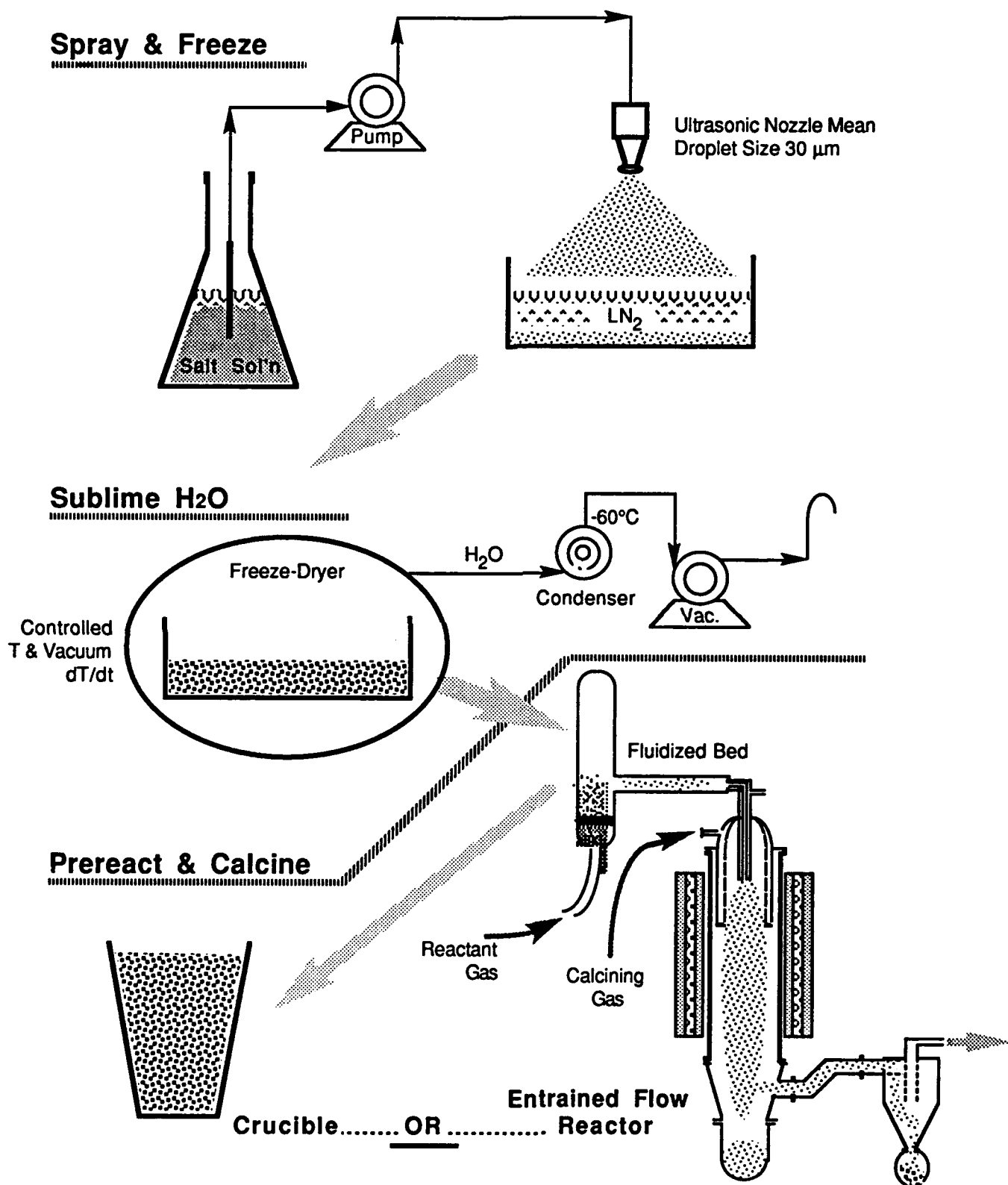
Place trays in cooled freeze-dryer after majority of LN has evaporated.

Temperature range: -35°C to $+40^\circ\text{C}$, ~ 24 hours.

Further Treatment

Ball-mill dried precursor powder for 15 minutes with ZrO_2 media.

Calcine, press, and sinter powder.



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Figure 1. Freeze-drying process.

Solution Preparation

YBCO Powders. Initial batches of YBCO powders were prepared from solutions of $\text{Y}(\text{NO}_3)_3$, $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, and $\text{Cu}(\text{NO}_3)_2$. Solutions of the desired concentration were prepared from the salts (Table 1) dissolved in distilled water. The solutions were heated to $50^\circ\text{--}100^\circ\text{C}$ to aid in dissolution of the salts. The overall solution concentration was 0.13 molal, and the pH was adjusted to 3-4 with NH_4OH .

We studied the effects on pH of the order of addition of the solutions to the mixture and we determined the amount of NH_4OH required to reach a specific pH.

Although the powders prepared in the initial part of this study had the desired stoichiometry, some later powders were off-stoichiometry. The starting salts were found to have variable compositions, particularly with regard to the numbers of water of hydration. The decline in quality was probably associated with the large increase in demand experienced by the commercial suppliers for these salts. A new procedure for solution preparation was developed.

Yttrium nitrate solutions prepared from the salt were analyzed for cation concentration by volumetric techniques involving titration with ethylenediamine tetraacetic acid (EDTA). End-point indicators included eriochrome black T, xylene orange, and murexide. Volumetric analysis procedures were derived from standard techniques.¹¹ Copper nitrate solution was prepared by dissolving high purity copper in excess HNO_3 . Nitrate solutions were mixed before the addition of Ba acetate. Because barium acetate solutions absorb CO_2 from the atmosphere to form BaCO_3 , barium acetate was added to the solutions just before the addition of NH_4OH to adjust the pH and spraying. The solution was kept covered and sprayed immediately.

Procedures for titration are given in Appendix A.

Spraying

Solutions were sprayed into trays of liquid nitrogen in a hood using an ultrasonic sprayer. The nozzle produced droplets of approximately 30- μm diameter. The spraying rate was 4 L/hour. One liter of solution was sprayed into each tray (~18 in. x 12 in. x 1 in.). The trays were placed on foam insulating material, and the liquid nitrogen was allowed to quiesce before spraying. More liquid nitrogen was added as needed during spraying to keep the trays full. Droplets that contacted others tended to form agglomerates in the form of rafts, which were broken up continuously with rubber spatulas during spraying.

The trays were kept full of liquid nitrogen (LN) until all spraying into all trays was complete. Most of the LN was allowed to evaporate before the trays were placed in the freeze-dryer.

Some variations on spraying included spraying into a stirred dewar of LN and blending the frozen material before drying. Both approaches were taken to decrease the agglomeration of the frozen droplets. The effects of these spraying techniques on the surface area was determined.

Freeze-Drying

Two freeze-dryers (see Table 2) were used in this study. Only YBCO powders were dried in the large 4-tray dryer to ensure that there was no contamination. There is no significant difference in the operation of the two machines. The trays and chambers were cleaned between uses.

A freeze-dryer in the tray configuration consists of a chamber with shelves for the trays, a condenser and associated pumps, heat transfer liquid reservoirs, and temperature and vacuum controllers. The shelves are cooled/heated with a heat transfer fluid. In this work, we used corrosion-resistant freeze-dryers with condenser temperatures of -84°C and shelf temperature range of -50°C to $+50^{\circ}\text{C}$. The trays are clamped to the shelves to aid in heat transfer.

The shelves were cooled before the trays were inserted. Thermocouples were inserted directly into the frozen material to monitor product temperature. The vacuum was applied after most of the LN had evaporated. The temperature of the frozen product increased to the shelf temperature in approximately 50 minutes and was then controlled at a programmed ramp rate to the maximum temperature.

In a commercial process, it is important to minimize the time spent in the freeze-dryer. In the laboratory, however, it was convenient to have freeze-dryer runs of ~ 24 hours. Several freeze-drying programs were used; a typical run is shown in Table 4. The maximum temperature was $\sim 35^{\circ}\text{C}$.

Table 4
Typical Freeze-Drying Program

Segment	Temperature (°C)	Time (hr)	Ramp Rate (°C/min)
1	-196 to -60	2	1.1
2	-60 to -10	4.2	0.2
3	-10 to -10	1	0
4	-10 to 10	3.3	0.1
5	10 to 10	1	0
6	10 to 35	1	0.4
7	35	10	---

Powder Handling and Milling

The dried material (precursor powder) was removed from the freeze-dryer as rapidly as possible to prevent rehydration and atmospheric contamination. It was stored in sealed polyethylene jars under an inert atmosphere.

The precursor powders were ball-milled with ZrO_2 balls in the sealed jars at low speed for 15 minutes to break up the agglomerates. The precursor was stored in the sealed bottles until calcination.

A series of experiments was performed to determine the effects of ball milling calcined powders on the surface area and the critical current density. Calcined powders were milled both dry and with ethanol. Powders milled in ethanol were dried before pressing.

Heat Treatment

Calcining. Several approaches to calcining were used. At first, the precursor powder was placed in heated ($\sim 100^\circ\text{C}$) 500- and 750-mL Al_2O_3 crucibles and placed in a 300°C furnace. Powders were also calcined in shallow Al_2O_3 trays. The atmosphere was flowing O_2 .

YBCO powders were generally calcined at 825°C , although we also conducted a series of experiments to determine the effects of other calcining temperatures on powder properties. Annealing at 550°C was usually performed after sintering. Again, various annealing times and temperatures were used.

The improvements in the calcining procedure leading to the synthesis of carbonate-free powders are described in Section 5. The development of the technique is regarded as one of the most important results of this project. The basis and description of the technique and the characterization of powders calcined by this technique are included as a separate section of this report to emphasize the importance of this development.

Calcined powders were stored in sealed jars under inert atmosphere.

Sintering. The calcined powders were usually die pressed into pellets or discs. Small pellets of 4- to 7-mm diameter and 1- to 2-mm height were sintered for T_c measurements. Larger discs (~8-10 mm in diameter) were prepared and cut into thin pieces <1-mm thick for transport current measurements. The largest discs (~500 mm in diameter and ~4 mm in height) were prepared for use as sputtering targets by Stanford University.

YBCO samples for sintering were placed on YBCO powder on Al_2O_3 substrates or occasionally on Pt wire. The sintering conditions for YBCO material were usually 890°C for 24 hours, followed by annealing at 550°C for 24 hours in flowing O_2 . A series of experiments was conducted to determine the effects of sintering times and temperatures on the superconducting properties.

3. CHARACTERIZATION AND EVALUATION

Superconducting properties such as critical current density and transition temperature were originally evaluated at Stanford University. In the latter part of the program, critical transition temperature measurements were performed at SRI using a technique similar to that used at Stanford.

TRANSITION TEMPERATURE MEASUREMENT

Transition temperatures were measured using a standard four-point resistivity technique on samples of 4- to 12-mm diameter. Silver paint (from a conductive pen) was used to form the four electrical contacts on the samples. Samples were placed at the tip of the probe and contact made with thin phosphor bronze wires. The sample was then lowered slowly into a dewar of liquid nitrogen (or liquid helium), and the resistivity was measured as a function of temperature, using the appropriate electronics. The dipping time from room temperature to $\sim 77\text{K}$ was 30 to 40 minutes.

Calibration runs were performed using the same samples at SRI and Stanford to ensure that the SRI equipment built in the latter part of the program gave results that agreed with those from Stanford. Samples were cut or sanded to be flat, to have the correct dimensions to fit in the probe, and to remove any insulating layer that may have formed during storage before testing.

CRITICAL CURRENT DENSITY

Critical current density measurements were made at Stanford University. Most measurements were made by a DC magnetization method and the Bean approximation. In the early part of the program, transport measurements were made on several samples. Stanford University has verified that the results obtained by transport measurements and magnetic measurements are in agreement.

Critical currents were measured as a function of applied field by measuring the induced saturation magnetic moment on a vibrating sample magnetometer attached to a magnet capable of generating a field up to 18 kG. The DC moment was measured by ramping the field to a certain value, allowing the moment to decay for 1 second, and then measuring the sample moment. The Bean formula

$$J_c(H) = 30 \Delta M(H)/VR$$

was used to determine the critical current $J_c(H)$ as a function of applied field H from the observed hysteric moment $\Delta M(H)$; V is the sample volume and R is the sample radius.

Stanford University compared the critical current densities measured by magnetization and by transport and found the results equivalent for the two methods.

MATERIAL CHARACTERIZATION

The density of sintered samples was determined by measuring the dimensions and weighing. Archimedean techniques were not used, to avoid contaminating the samples. Microstructure was examined by scanning electron microscopy. Compositional analyses were determined by EDAX and by inductively coupled plasma techniques (ICP, courtesy of Stanford University). Surface areas were determined by BET. Powders, bulk materials, and powdered bulk materials were subjected to X-ray diffraction for phase analysis. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to study calcination of the freeze-dried material and phase purity of the calcined material, respectively. TGA was performed in N_2 , and DTAs were performed in both N_2 and O_2 .

4. POWDER SYNTHESIS RESULTS AND DISCUSSION

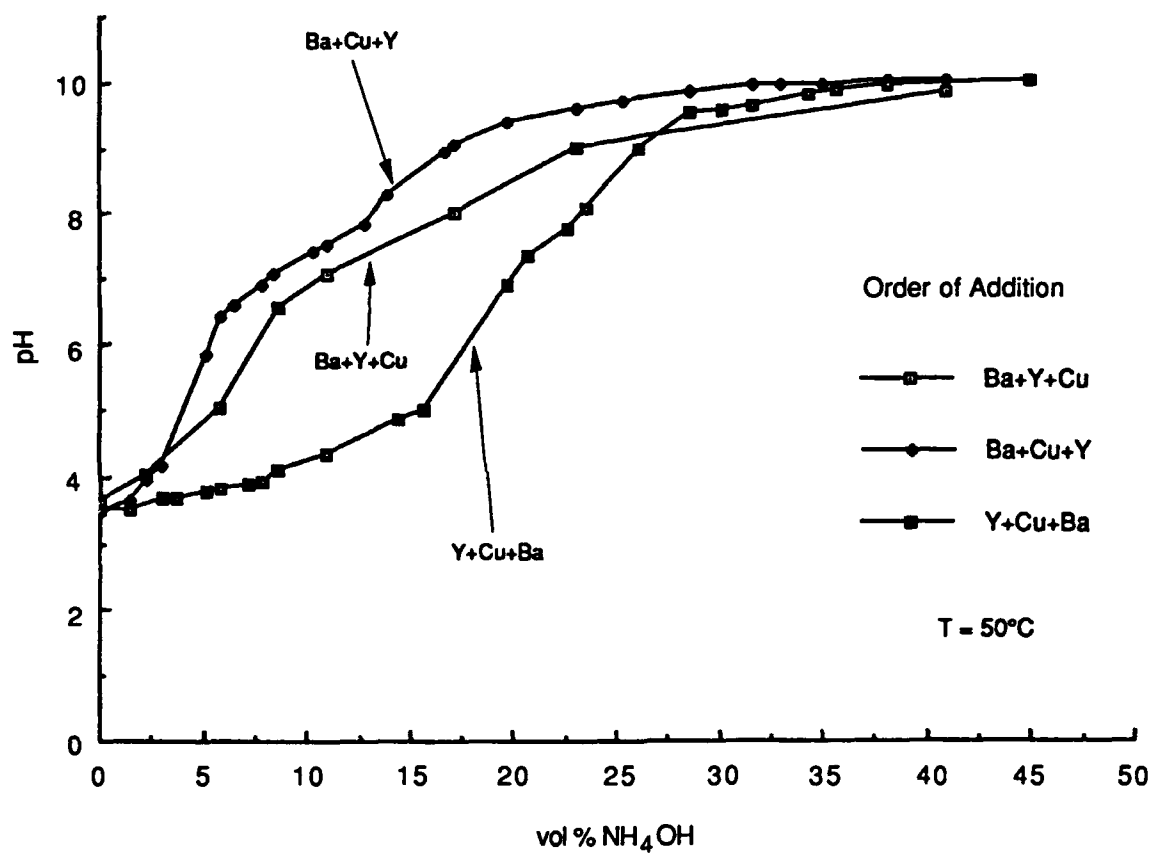
Only the results of the first part of the program are discussed here. These include the results of experiments made on the synthesis technique and on powders made using the original calcination approach. The development and results of evaluation of powders prepared by the new calcination technique are given in Section 5.

Table 5 gives details of the materials, transition temperatures, surface area, phase analysis, and comments on the sample preparation and sintering conditions. The final techniques for powder synthesis were based on previous experience and modifications to the procedure made after analysis of the powders. Table 6 lists the synthesis variables found to be important in freeze-drying. These considerations are applicable in varying degrees to the synthesis of any powders by freeze-drying.

PRECIPITATION

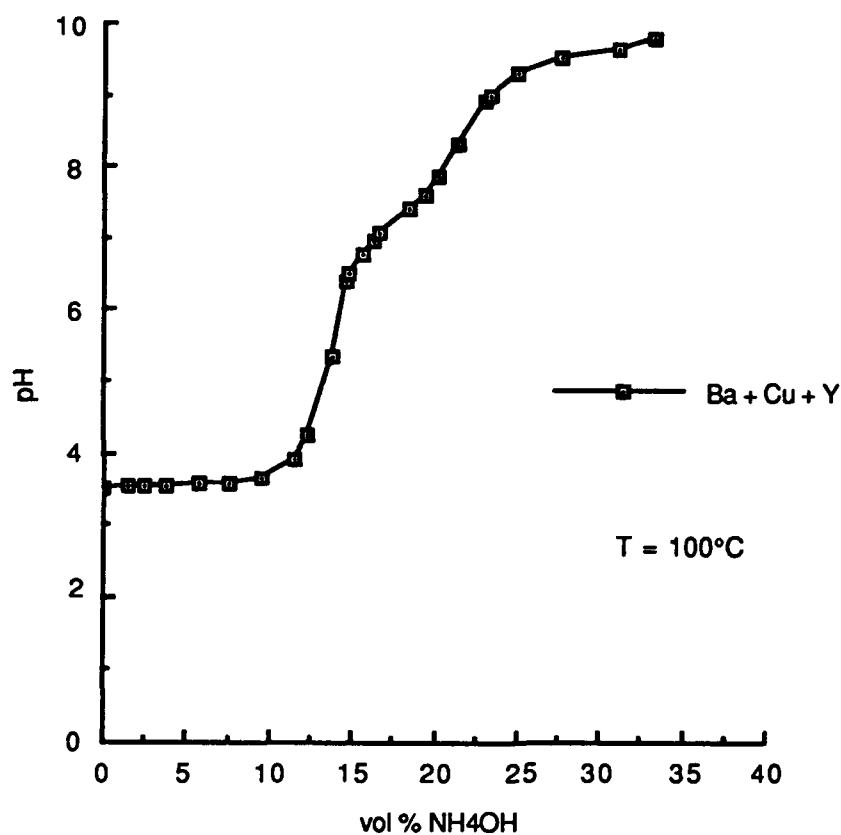
Ideally, for producing a very homogeneous powder, the solutions to be used for freeze-drying should contain no precipitates. However, avoiding precipitates is often not possible in multicomponent systems for which there are a limited number of soluble salts, a choice that is limited further by the common anion effect and by reactions between the salts. For example, if Y nitrate and Cu nitrate are used to prepare YBCO compounds, Ba nitrate cannot be used because it has a low solubility and the common anion effect causes severe precipitation. Barium acetate can be used in this synthesis.

A study was made to determine if the order of mixing of the solutions had any effect on the chemistry. The solutions were mixed in different orders, and the pH was determined as a function of the amount of NH_4OH added. Figure 2 shows the effects of order of addition on the pH (for solutions at 50°C). The effect of increasing the temperature is shown in Figure 3. Although the pH rises more rapidly in solutions made by adding the nitrates to the Ba acetate, the pH of all systems is similar at low and high temperatures. The effect of temperature on the Ba plus nitrate solutions is to maintain the pH at a low value over a wide range of NH_4OH and to give higher solubilities for the salt additions. Order of mixing is not important in controlling the pH. As discussed later, however, the order of mixing is important in controlling BaCO_3 contamination. The acetate solution will absorb CO_2 from the atmosphere. Ba acetate should be added to solutions just before spraying.



RAM-6585-27

Figure 2. Effect of order of addition of salts on the pH of the solutions at 50°C .



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Figure 3. Effect of increasing temperature (100°C) on the variation of pH with volume of NH_4OH .

Table 5
CONDITIONS FOR POWDER PREPARATION

Powder	Method	pH	°C	(m ² /g)	K	YBCO plus	Comments
DP1-18	Nitrates + Ba(Ac)	4.02	825	4.4	—	«CuO	—
DP2a-43	Ba(Ac) + Nitrates (Y then Cu)	3.75	825	3.7	—	«CuO; «Y ₂ O ₃	No NH ₄ OH; sprayed @ 65°C
DP2b-43	Ba(Ac) + Nitrates (Y then Cu)	8.79	825	3.2	—	«CuO; «Y ₂ O ₃	Sprayed @ 65°C
DP2c-43	Ba(Ac) + Nitrates (Y then Cu)	3.78	825	4.4	—	«CuO; «Y ₂ O ₃	Sprayed @ 53°C
DP3a-43	Ba(Ac) + nitrates (Cu then Y)	3.64	825	—	—	—	No NH ₄ OH; sprayed @ 53°C
DP3b-43	Ba(Ac) + nitrates (Cu then Y)	8.63	825	—	—	—	Sprayed @ 65°C
DP3c-43	Ba(Ac) + nitrates (Cu then Y)	3.95	825	—	—	—	Sprayed @ 53°C
DP4a-43	Nitrates (Y then Cu) + Ba(Ac)	3.73	825	—	—	—	No NH ₄ OH
DP4b-43	Nitrates (Y then Cu) + Ba(Ac)	8.67	825	—	—	—	—
DP4c-43	Nitrates (Y then Cu) + Ba(Ac)	4.06	825	4.0	—	—	—
DP5-48	Ba(Ac) + Nitrates (Y then Cu)	3.41	825	3.0	—	—	Solution mixed and sprayed at 100°C
DP6a-48	Ba(Ac) + Nitrates (Cu then Y)	9.77	825	—	—	—	Mixed and sprayed at 100°C
DP6b-48		3.51	825	—	—	—	—
DP7-48		3.53	825	3.2	—	—	Mixed and sprayed at 100°C
DP8-67		3.86	825	3.6	80	«CuO; «Y ₂ O ₃	Mixed and sprayed at 50°C
DP9-20		3.87	830	4.1	82		ICP{Y _{1.08} Ba _{1.92} - Cu _{2.99} }

<< = Small percentage

† = Mixing of 3 separate stock solutions

* = Separate Cu & Y solutions; Ba added last in powder form.

Table 5 (Continued)

Powder	Method	pH	°C	(m ² /g)	K	YBCO plus	Comments
DP10-12	Ba(Ac) + Nitrates (Y then Cu)	4.00	810	4.0	68	«211 phase	
DP11-20	(Cu ^o +HNO ₃) + Ba + Y	4.00	827	1.7	—	—	
DP12-14	(Cu ^o + HNO ₃) + Ba + Y	4.63	825	4.2	—	—	—
DP13-12	†(Cu ^o + HNO ₃) + Ba + Y	4.53	825	—	—		ICP{Y. ₉₈ Ba _{2.02} Cu _{2.97} }
DP13- 12MQ		—	890	0.8	62	«211 phase; «Y ₂ O ₃	Powder DP13-12 annealed an additional 40 hr @ 890°C
DP14-12	†(Cu ^o + HNO ₃) + Ba + Y	4.23	825	1.3	65	BaCO ₃ ; 211; CuO	ICP{Y. ₉₉ Ba _{2.02} Cu _{2.97} }
DP15-84	†(Cu ^o + HNO ₃) + Ba + Y	4.14	825	1.7	-	BaCO ₃ ; 211; CuO	
DP16	† (Cu ^o + HNO ₃) + Ba + Y	4.08	—	—	—	—	Product melted during freeze-drying (Equipment failure)
DP17-42	*(Cu ^o + HNO ₃) + Ba + Y	4.03	825	2.2	87	Clean 1-2-3	—
DP18-24	Acetates (Ba+Cu) + Y (Nitrate)	4.76	825	1.6	80	—	Small amount of yellow precipitate; dark black calc. powder
DP19-18	*(Cu ^o + HNO ₃) + Ba + Y	4.52	825	—	79	«2-1-1 phase	Blended frozen product
DP19-04		4.52	825	—	83	Clean 1-2-3	Non-blended frozen product
DP20-01	*(Cu ^o + HNO ₃) + Ba + Y	5.35	510	2.8	89	—	—
DP20-03	*(Cu ^o + HNO ₃) + Ba + Y	5.35	600	2.2	semi- cond.	—	—
DP20-13	*(Cu ^o + HNO ₃) + Ba + Y	5.35	650	4.5	85	—	—

<< = Small percentage

† = Mixing of 3 separate stock solutions

* = Separate Cu & Y solutions; Ba added last in powder form.

Table 5 (Continued)

Powder	Method	pH	°C	(m ² /g)	K	YBCO plus	Comments
DP20-07	*(Cu ^o + HNO ₃) + Ba + Y	5.35	700	3.1	85	—	—
DP20-15	*(Cu ^o + HNO ₃) + Ba + Y	5.35	750	1.6	91	—	—
DP20-09	*(Cu ^o + HNO ₃) + Ba + Y	5.35	800	1.8	74	—	—
DP20-19	*(Cu ^o + HNO ₃) + Ba + Y	5.35	825	2.3	72	—	—
DP20-05	*(Cu ^o + HNO ₃) + Ba + Y	5.35	835	2.2	83	—	—
DP20-17	*(Cu ^o + HNO ₃) + Ba + Y	5.35	853	1.2	91	—	—
DP20-21	*(Cu ^o + HNO ₃) + Ba + Y	5.35	868	1.2	88	—	—
DP20-23	*(Cu ^o + HNO ₃) + Ba + Y	5.35	875	2.0	semic ond.	—	—
DP20-11	*(Cu ^o + HNO ₃) + Ba + Y	5.35	895		76	—	—
DP20-25	*(Cu ^o + HNO ₃) + Ba + Y	5.35	908	0.4	85	—	—
DP21	*(Cu ^o + HNO ₃) + Ba + Y	2.85	—	—	—	—	Melted during freeze-drying (equipment failure)
DP22	*(Cu ^o + HNO ₃) + Ba + Y	3.21		—	—	—	90% melted during freeze-drying
DP23	*(Cu ^o + HNO ₃) + Ba + Y	3.65	825	4.9			
DP24	*(Cu ^o + HNO ₃) + Ba + Y	3.74	825	2.4			Blended frozen product; minimum air contact
DP25	*(Cu ^o + HNO ₃) + Ba + Y	3.88	914				Blended frozen product; NH ₄ OH trap for sintering

<< = Small percentage

† = Mixing of 3 separate stock solutions

* = Separate Cu & Y solutions; Ba added last in powder form.

Table 5 (Concluded)

Powder	Method	pH	°C	(m ² /g)	K	YBCO plus	Comments
DP26	*(Cu° + HNO ₃) + Ba + Y	4.08	914		88		1Y-1.2Ba-2.2Cu— (5Y-6Ba-11Cu-4Oxy); Blended frozen product; NH ₄ OH trap for sintering
DP27	*(Cu° + HNO ₃) + Ba + Y	4.27	825		77		Blended freeze- drying material; calcined in alumina trays
DP28	*(Cu° + HNO ₃) + Ba + Y	3.85	825				Calcined in alumina trays
DP28Q	*(Cu° + HNO ₃) + Ba + Y	3.85	893				Calcined & annealed in alumina trays; green phase evident
DP29	*(Cu° + HNO ₃) + Ba + Y	4.22	825				
DP30	*(Cu° + HNO ₃) + Ba + Y	4.06	825				
DP31	*(Cu° + HNO ₃) + Ba + Y	4.00	825				
DP32	*(Cu° + HNO ₃) + Ba + Y	4.13	825	3.3			1Y-2Ba-2.4Cu
DP33	*(Cu° + HNO ₃) + Ba + Y	4.04					
DP34	*(Cu° + HNO ₃) + Ba + Y	4.39					
DP35	*(Cu° + HNO ₃) + Ba + Y	4.47					
DP36	*(Cu° + HNO ₃) + Ba + Y	4.35					
DP37	*(Cu° + HNO ₃) + Ba + Y	4.55					1Y-4Ba-3Cu, barium- rich
DP38	*(Cu° + HNO ₃) + Ba + Y	4.42					
DP39	*(Cu° + HNO ₃) + Ba + Y	3.46					
DP40	*(Cu° + HNO ₃) + Ba + Y	3.54					

<< = Small percentage

† = Mixing of 3 separate stock solutions

* = Separate Cu & Y solutions; Ba added last in powder form.

Table 6
Synthesis Variables vs Process Needs and Rationale

<u>Variable</u>	<u>Rationale</u>
Type of salt	High solubility, purity, controlled stoichiometry, common anion effect, chemically compatible on heat treatment
Solution concentration	High to maximize yield, low for very fine particles
pH	Control for solubility, freeze-drying capability
Temperature of solution	Higher solubility of salts
Spraying conditions	Balance rate versus droplet size and agglomeration
Drying conditions	Minimum time, maximum starting temperature to maintain powder form
Milling	Minimum time and speed to avoid contamination
Calcining conditions	Minimum time consistent with avoiding melting, explosive situations, and agglomeration
Handling	Avoid contamination

CONCENTRATION

A high concentration of the salts in the solution is desirable both to give a high yield of powder and to minimize the amount of water that must be removed during drying. However, the limited solubility of salts and the interactions among the components in the solution limit the concentration. A solution concentration of 0.13 m was used to prepare YBCO powders.

pH VALUES

When nitric acid is used to dissolve copper, the resulting solution has a very low pH. Although the solution does not contain precipitates and can be sprayed, it cannot be dried by evaporation. Solutions (with a very low pH) are vacuum treated to evaporate the solvent, the residue melts to form a glassy material at very low temperatures before it is completely dry. Further evacuation of the chamber does not result in significant further drying because very little surface area is exposed.

The explanation for this behavior lies in the eutectic between $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$ and ice (at 12.2 mol% HNO_3 and -43°C).¹² When the solution is heated from LN temperature, water is removed preferentially because it has a higher vapor pressure than HNO_3 . On reaching the eutectic temperature, part of the frozen solution starts to melt. The extent of melting depends on the initial concentration and the pH. The mixed solution is very complex chemically, and many species are formed, some of which have very low melting points, contributing to the melting problem.

Neutralizing the solution with NH_4OH before spraying produces solutions with higher pHs that do not melt during the freeze-drying because the HNO_3 is bound in NH_4NO_3 (melting point $\sim 170^\circ\text{C}$). However, the high pH can result in the precipitation of hydrolysis products. In practice, solution concentrations and pH values must be chosen to balance the formation of precipitates in the solution to be sprayed and the tendency to melt during freeze-drying.

SPRAYING

Solutions can be sprayed by several techniques, including aerosol generators, which produce submicron droplets, and ultrasonic sprayers, which produce larger droplets. Aerosol generation require fast gas flows and generates droplets that follow dynamic lines and therefore, may not impact on the cold surface. Ultrasonic sprayers do not require gas flows and therefore are more adequate for our purpose. Furthermore, ultrasonic sprayers have larger throughput. Spraying sufficient quantities to obtain large yields of powder requires the use of an ultrasonic sprayer. Approximately 4 liters of solution can be sprayed in 1 hour using an ultrasonic sprayer, which produces droplets of $\sim 30\text{-}\mu\text{m}$ diameter.

FREEZE-DRYING

The freeze-drying time should be as short as possible, compatible with the prevention of melting. Most materials can be dried in ~ 24 hours in a laboratory size freeze-dryer. The dried material has a fluffy appearance, is hygroscopic, and is kept under an inert atmosphere.

STOICHIOMETRY/CONTAMINATION

Although the contamination and stoichiometry problems were solved by careful handling and analysis, there were still some problems associated with agglomeration at the end of the program.

The best results were obtained when Cu nitrate solutions were prepared by dissolving high purity copper in HNO_3 , avoiding the problem of inconsistent number of waters of hydration on

commercial salts. Addition of Ba acetate at the last minute and careful handling solved the problem of BaCO₃ contamination from these sources. Analysis of solutions is crucial for obtaining the desired stoichiometry. Careful handling and storage of precursors and powders are also required.

Surface analysis by laser ionization (SALI) was used to perform a depth profile on a sintered sample early in the program. The sample was fractured just before testing to preferentially expose the grain boundaries. A Ta₂O₅ standard was used to estimate the sputtering depth; the depths given in Table 7 are the equivalent depths for this standard. The relative signals of the photo ions of Y, Ba, Cu, BaO, and BaOH were monitored as a function of depth and are given in Table 7 relative to Ba; these are raw signals not calibrated to give the correct stoichiometries. The spot size was 50 μ m. The surface is rich in Y and Cu and contained BaOH to a significant depth. This result shows that care needs to be taken to prevent exposure to the atmosphere.

TABLE 7
Signals for Individual Species as a Function of Depth, Obtained from SALI

Depth (Å)	Y	Ba	Cu	BaO	BaOH
Surface area	0.17	1	0.85	0.12	0.05
5	0.14	1	0.76	0.12	0.06
15	0.18	1	0.87	0.13	0.06
30	0.20	1	0.90	0.12	0.06
50	0.23	1	0.94	0.13	0.06
150	0.33	1	0.98	0.12	0.04
3200	0.45	1	1.08	0.12	0.01

A major source bulk of BaCO₃ contamination is the calcination technique. the calcination technique used at the beginning of the program is discussed later in this section. Improvements in the calcination technique are discussed in Section 5.

AGGLOMERATION

Agglomeration arises from three sources. Frozen droplets float on the surface of the LN after spraying and new droplets can stick to them. Partial melting during freeze-drying can lead to sticking or the formation of larger droplets. However, the hardest agglomerates are formed during calcination if there is any melting of the precursor phases or sintering of the particles during long heat treatments.

The first source of agglomeration was addressed by spraying into a stirred LN bath in an effort to remove droplets from the surface before new ones landed on them. Some LN/droplet mixtures were also blended in a laboratory blender before drying. However, the best approach to breaking up the agglomerates at this stage was found to be lightly ball-milling the freeze-dried material. The effects of deagglomeration treatments on the surface areas of powders calcined under various conditions are shown in Table 8. Pretreating the precursors clearly raises the surface area of the calcined powders from $\sim 2 \text{ m}^2/\text{g}$ to $\sim 4 \text{ m}^2/\text{g}$.

Table 8
Effect of Pretreatment and Starting Calcining Temperature
on Surface Areas of YBCO Powders

<u>Pretreatment</u>	Surface Area (m^2/g)			
	<u>100°C^a</u>	<u>200°C^a</u>	<u>300°C^a</u>	<u>400°C^a</u>
Blending ^b	4.4	3.5	4.5	3.7
Stirring ^c		3.5	3.4	4.0
Normal ^d		2.3		

Note: All powders are calcined at 825°C for 12 hours.

a. Starting temperature for calcining

b. Frozen material is blended before drying.

c. Solutions are sprayed into stirred LN.

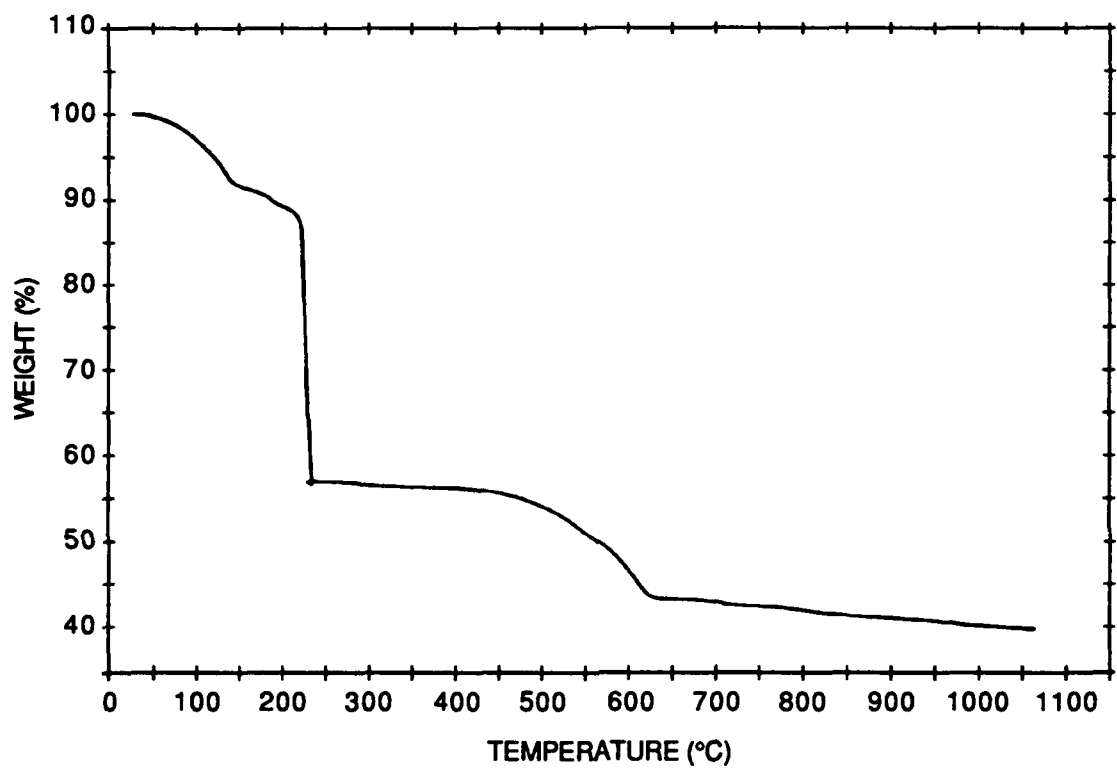
d. Solution is sprayed into LN in trays.

The second source of agglomeration can be avoided by controlling the pH of the solution and the drying profile. The third source of agglomeration is calcination and is discussed below.

CALCINATION/ANNEALING

Calcination is required to remove volatile species and to react the oxides to form the superconductor. Annealing to incorporate oxygen in the structure is usually performed after sintering.

A TGA scan for the YBCO freeze-dried precursors is shown in Figure 4. Weight loss begins around 100°C for the YBCO precursor with a major weight loss at $\sim 200^\circ\text{C}$ and a second smaller loss between $\sim 450^\circ$ and 600°C . Weight loss is essentially complete by 600°C . The initial weight loss near 100°C is probably related to residual moisture in the powders and the retention of



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Figure 4. Thermogravimetric analysis of freeze-dried YBCO precursor (N₂).

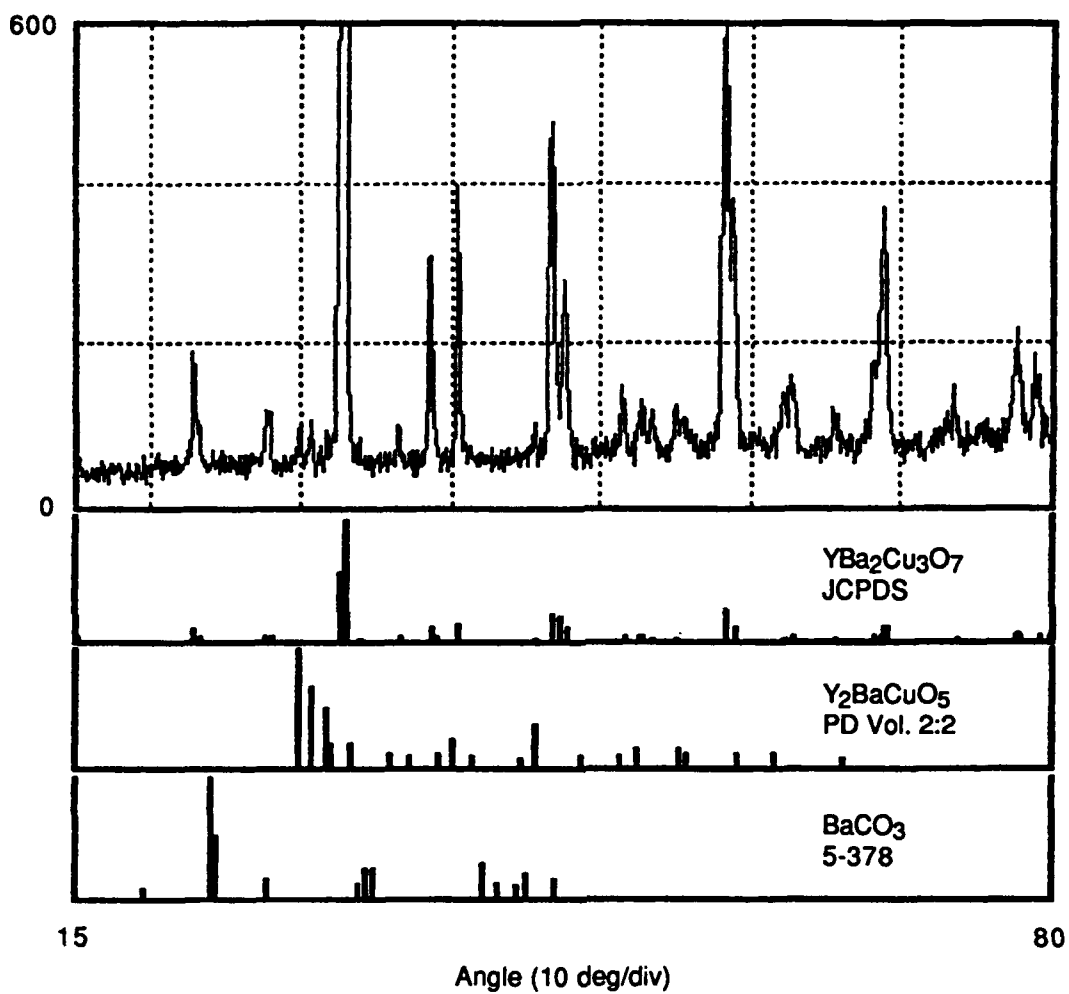
some of the water of hydration. $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, for example, loses $3\text{H}_2\text{O}$ at $\sim 100^\circ\text{C}$. $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ loses $3\text{H}_2\text{O}$ at 26°C (during freeze-drying) and HNO_3 at 170°C . The hydrated form of barium acetate loses water at 150°C . The first weight loss is probably associated with the loss of water, species such as HNO_3 , and as discussed below, species containing carbon. The higher temperature weight loss is probably associated with the decomposition of nitrates. For example, below 223°C , $\text{Cu}(\text{NO}_3)_2$ mostly volatilizes as a molecule, above 223°C , the solid decomposes to form NO_2 and O_2 . $\text{Ba}(\text{NO}_3)_2$ does not decompose to NO_2 and O_2 appreciably up to $T > 525^\circ\text{C}$.

Table 9 shows the effect of the final calcining temperature on the surface area of YBCO powders. Surface area decreases dramatically with higher calcining temperatures because of sintering of the highly active particles. The material calcined at the lower temperatures is not single-phase. However, enough of the correct phase is produced on sintering to result in values of T_c close to 90K for all samples.

Table 9
Effects of Calcining Temperature on Surface Area on YBCO Powders

<u>Calcining Temperature ($^\circ\text{C}$)</u>	<u>Surface Area (m^2/g)</u>
650	4.5
700	3.1
750	1.6/2.4
800	1.8
825	2.3
853	1.2
868	1.2
908	0.4

An XRD pattern of a calcined powder is shown in Figure 5. Although only the 123 phase is indicated, XRD does not show low levels of carbonate. As discussed in the next section, differential thermal analysis is necessary to identify small amounts of carbonate contamination.



RAM-4193-30

Figure 5. XRD scan of calcined $\text{YBa}_2\text{Cu}_3\text{O}_7$ powder (original calcination method).

CHARACTERIZATION AND EVALUATION

One of the goals of this work was to synthesize superconductor powders that yield materials with desirable superconducting properties. A parallel program¹⁰ had the goal of improving critical current density. The discussion of microstructure and superconducting properties in this section includes a brief discussion of results from the other program that proved beneficial to this program.

Microstructure

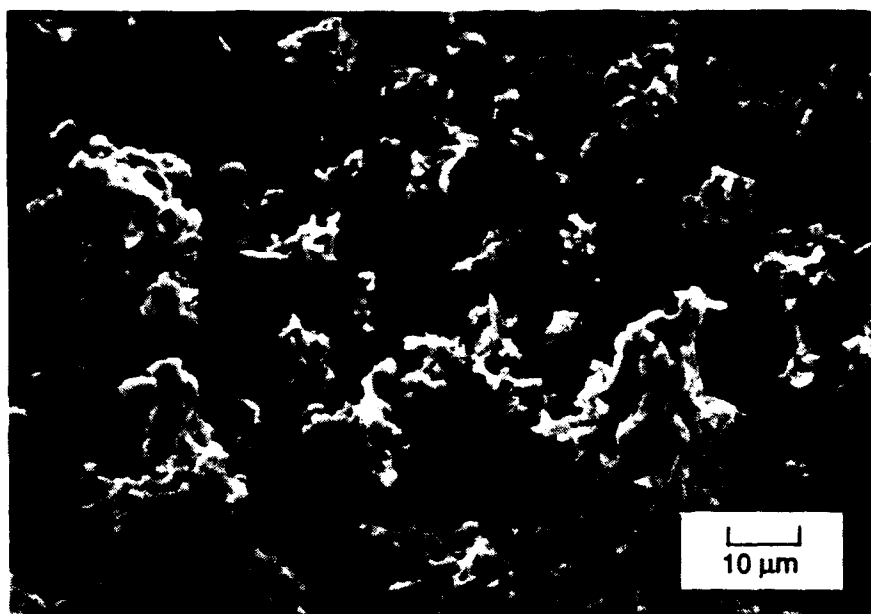
The dried, unreacted precursor is shown in Figure 6. Beads of $\sim 30\text{ }\mu\text{m}$ diameter were formed on spraying. On drying, these beads break up into smaller agglomerates of fine particles. The appearance of the powder depends on milling and calcining conditions. An example of powder calcined at 825°C is shown in Figure 7. The powder consists of agglomerates of sub-micron particles. The fine microstructure of the calcined agglomerates is also shown in Figure 8.

As noted above, the powder can be milled after drying, but before calcination while it is still soft. Agitation during spraying, milling, and calcining all affect the surface area as shown in Table 9 (above). Milling the powder before or after calcination will break up the agglomerates and increase the surface area.

The powders are very active and the surface area decreases significantly with increasing calcination temperature. The powders will sinter at 890°C to densities in excess of 90%. However, the final sintered density and microstructure are very dependent on the calcination and sintering conditions. A sintered microstructure is shown in Figure 9. This microstructure is porous but consists primarily of elongated grains. Porosity allows access of oxygen to the grains during annealing.

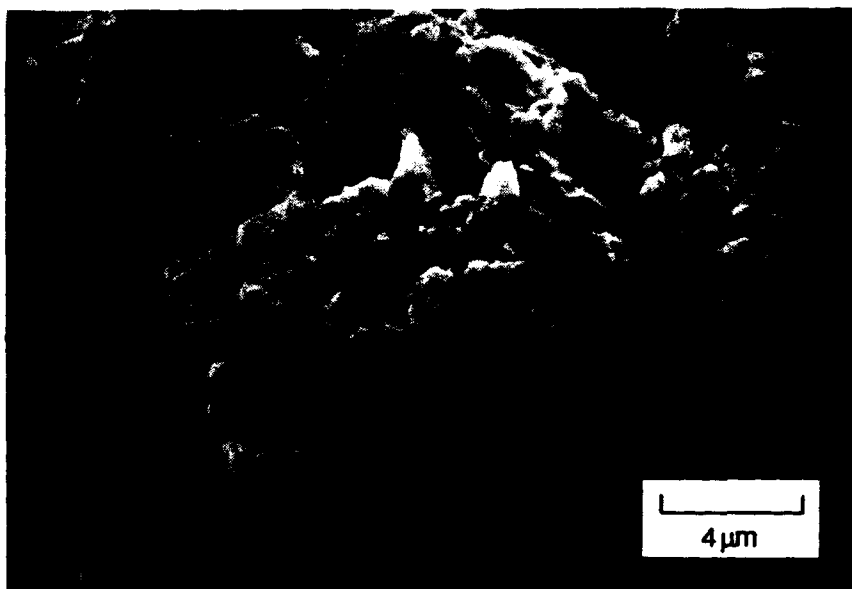
Superconducting Properties

a) Critical Transition Temperatures. Table 10 shows the effect of the calcining temperature of YBCO powders on the critical transition temperatures [midpoint (T_c), width (W), temperature difference between 10% and 90% of transition, and zero point ($T_p = 0$)] of materials sintered from the freeze-dried powders made in the first part of this program.



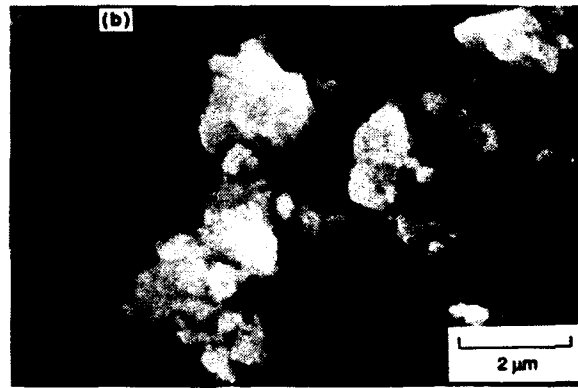
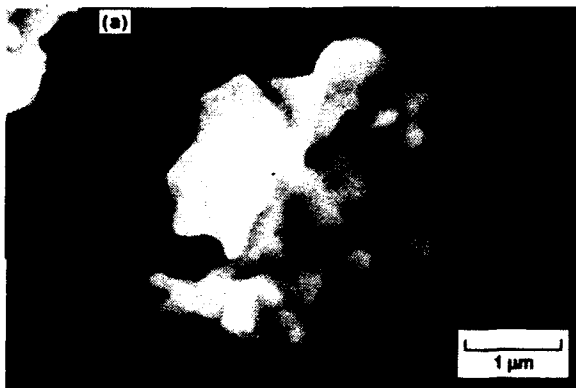
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Figure 6. Precursor after freeze-drying.



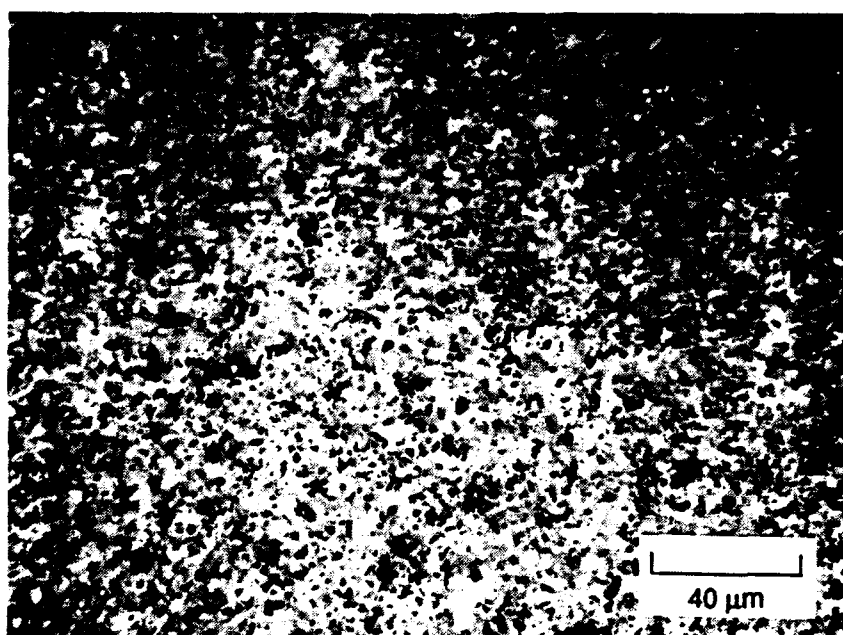
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Figure 7. Powder calcined at 825°C.



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Figure 8. Freeze-dried $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder.



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Figure 9. Microstructure of sintered freeze-dried $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder.

Table 10

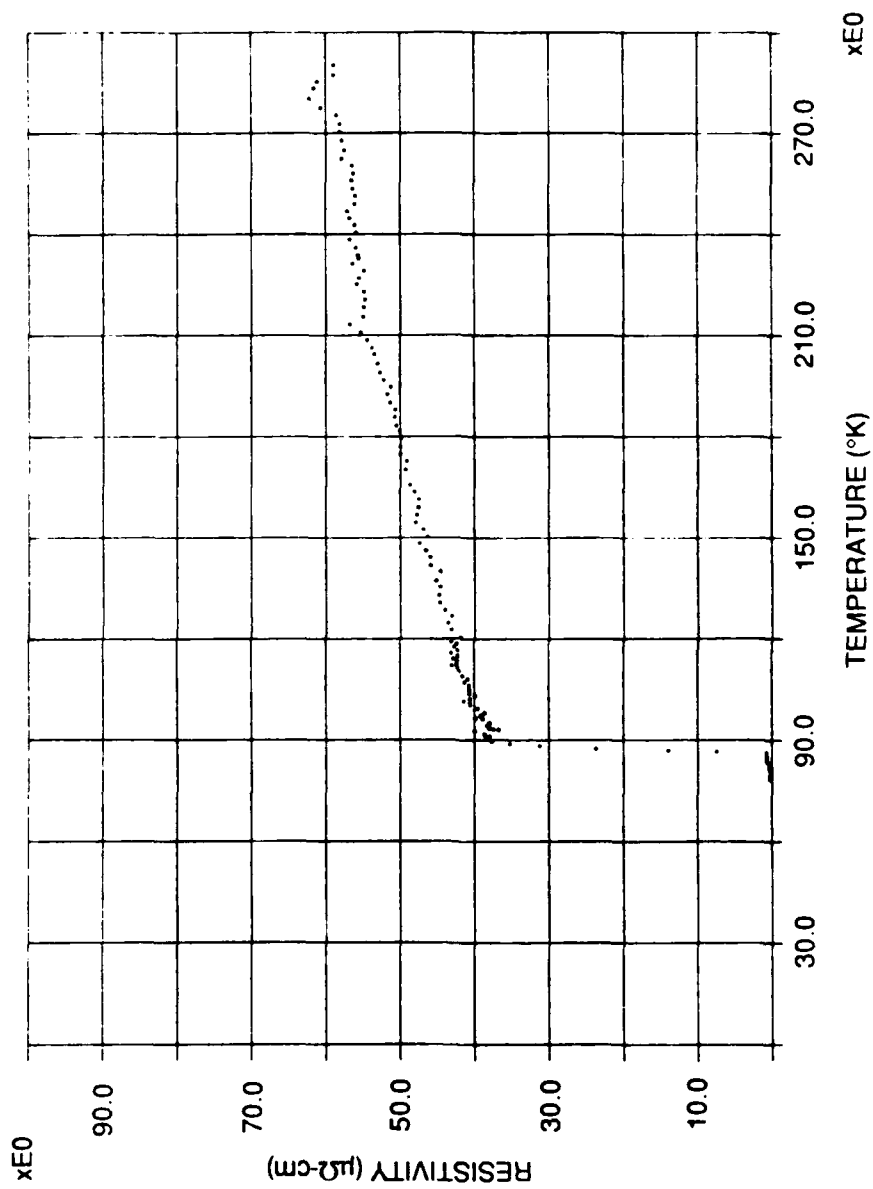
**Effects of Calcining Temperature on Critical Transition Temperatures
of Sintered Powders**

Calcining Temperature (°C)	T_c (K)	W (K)	T_{ρ = 0} (K)
650	90	6	86
700	91	6	86
750	92	2	91
800	85	12	75
825	89	10	80
853	93	5	92
868	91	15	88
895	89	10	80
908	90	4.5	86

The effects of calcining temperature on the critical transition temperature are not clear. The desired YBCO phase is not formed at the low temperatures, but clearly forms on sintering. The transition width appears to be narrower when powders are calcined at the lower temperatures. These powders were finer and thus more sinterable. Even after sintering, however, the material is not single phase. The highest T_c and narrowest transition were achieved with powders calcined at 750°C. We need to achieve a balance between (1) a calcining temperature low enough to produce a high surface area powder that will sinter to high density and thus have good grain-grain contact and (2) a calcining temperature high enough to produce the desired phase (but not so high as to cause melting). A typical temperature-resistivity curve is shown in Figure 10.

Critical Current Density. Various approaches were taken to improving the critical current density in YBCO-based materials. Table 11 shows the effects of processing variables including milling conditions and sintering times and temperatures on the critical current density of YBCO. Some of these data were gathered from another program, using powders made in parallel with this program, and are presented here to add completeness to this report. Also, J_c data from the improved powders produced by the two-stage calcination technique are included for comparison.

The processing experiments indicate that wet milling in ethanol is detrimental to the J_c, probably because of carbon contamination. Ethanol will vaporize cleanly at low temperatures. Although residual ethanol in powders heated rapidly to high temperatures during the calcining may result in the formation of CO₂ or residual C and thus the formation of BaCO₃, it is more likely that



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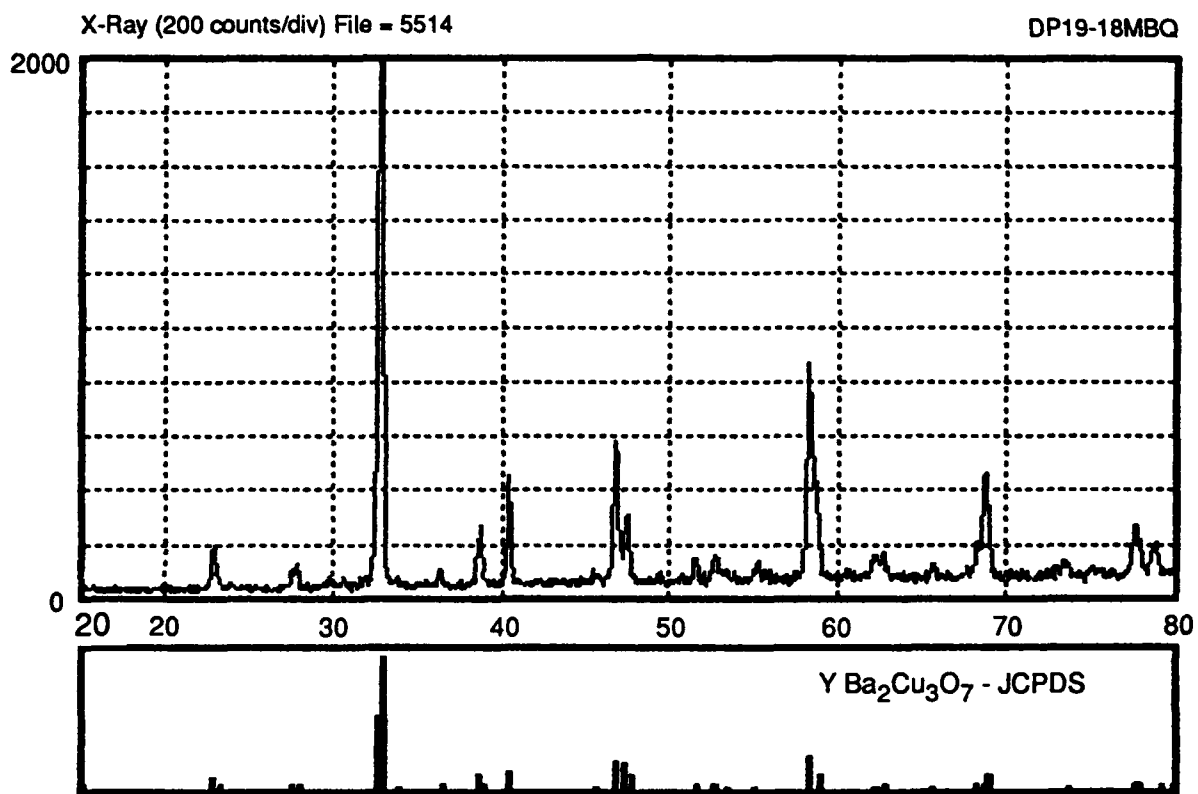
Figure 10. Typical temperature-resistivity curve for sintered sample.

the contamination arises from the drying process. The powders in these experiments were dried in air and may have absorbed CO_2 from the air. Carbon contamination from the calcination process, as described in the next section, is also responsible for low values of J_c .

Short sintering times and high sintering temperatures are also detrimental to the critical current density. Short sintering times do not result in full densification and good grain-to-grain contact, leading to low critical current density. High sintering temperatures, $>925^\circ\text{C}$, can lead to melting and consequent formation of nonsuperconducting phases. Samples sintered at 950°C had rough surfaces, indicating melting. A short time at 925°C does not appreciably affect the critical current density. The optimum sintering treatment for the freeze-dried YBCO powders is thus 890°C for 24 hours, followed by annealing at 550°C . The pellets formed under these conditions have densities in excess of 90%. Figure 11 shows the XRD pattern of a pellet sintered under these conditions and then ground up for analysis. The pattern is sharp and corresponds to the 123 phase, as shown by the reference lines. However, there may be residual carbon that is not detected by XRD. Other XRD analyses revealed carbon contamination, as did carbon analysis.

However, very slow cooling does appear to increase the critical current density, as indicated by samples 222 and 109. These samples also indicate the detrimental effect of wet milling. Slow cooling improves the J_c of wet-milled materials slightly, but the improvement is not as significant as that achieved with dry-milled powders. Slow cooling gives the highest J_c (6400 and 9200 A/cm^2 at 1.2 T and 0.5 T, respectively) achieved in powders not calcined by the improved, two-step calcination method. Slow cooling to the annealing temperature may allow more time for the incorporation of oxygen in the structure. However, Marucco et al.²² found it necessary to anneal at temperatures below 550°C to obtain an oxygen content of 6.85 to 6.9 in an annealing atmosphere of 1 atm of O_2 . Annealing at higher temperatures will not be effective in increasing the oxygen content of the material.

The beneficial effects of the two-stage calcination treatment on the J_c are also shown in Table 11. Sample FBR-7Q clearly demonstrates the improvements possible when all carbonate is removed from the material. Further detailed discussion of this technique is in the following section.



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Figure 11. XRD pattern of ground sintered sample.

Table 11

Effect of Processing Variables on Critical Current Density of YBCO Materials

Density Sample	Milling	Sintering Temperature (°C)/ Time (hr)	Critical Current (A/cm ² at 4.2 K)		Comments
			5 kG	12 kG	
101	M ^a	890/12	700	300	
102	M	890/12	700	300	
211	M	890/24	2,900	1,700	
212	M	890/24	2,600	1,500	
222	WM ^a	890/24	1,400	1,000	Slow cooling ^b
109	M	890/24	9,200	6,400	Slow cooling
229	WM	890/24	940	780	
230	M	890/24	900	620	
110	M	890/24	2,000	1,300	
234	WM	890/24	1,100	800	
215	M	925/3min ^c	2,000	1,000	
218	M	925/3min	1,700	1,000	
107	M	925/3min	1,500	800	
108	M	925/3min	1,800	1,400	
237	WM	950/6	270	190	
238	M	950/6	1,600	1,100	
111	M	950/6	550	270	
FBR-6Q		890/24	7,250	2-stage calcination ^d	
FBR-7Q		890/24	14,440	2-stage calcination	

^a M = dry milled, WM = wet milled in ethanol.

^b Treated at 925°C for 3 minutes following sintering at 890°C for 24 hours.

^c Slow cooled at 0.01°C/min from sintering temperature to annealing temperature (550°C).

^d Powder calcined in two stages to reduce BaCO₃ content.

BARIUM CARBONATE CONTAMINATION

Although the early results on the use of freeze-drying were encouraging and high purity YBCO powders were produced, later powders were found to be contaminated with BaCO_3 . The problem became acute as we attempted to scale-up the process. Calcining was originally performed in crucibles. The preparation of powders without significant contamination was probably the result of the generation of an NO_2 -rich atmosphere on decomposition of the nitrates. However, nitrate-acetate mixtures can be explosive because of the strong redox reactions that occur, and calcination in trays was viewed as a way of minimizing any explosive tendency by sweeping away the evolving gases immediately and not having large quantities of powder present. Unfortunately, it rapidly became apparent that the powders were contaminated with BaCO_3 and that explosions could still occur.

A vertical furnace with continuous feed-through of powder was used for calcination. The vertical furnace was thought to have the advantages of increased throughput, rapid calcination, minimization of particle growth/sintering during calcination, and minimization of the explosion hazard. It was believed that the explosive tendency could be harnessed to produce finer powders. However, powders produced in a vertical furnace proved to be very rich in BaCO_3 . The decomposition of the acetate and the flow conditions in the vertical reactor offered ideal conditions for formation of BaCO_3 .

We undertook a study to understand the decomposition of the precursors and to develop a calcination technique for avoiding carbon contamination, explosions, and particle coarsening. This study and the results are described in Section 5. The two-stage calcination technique described here is the most important result of this project and should find application for more than freeze-dried precursors to superconductors.

5. IMPROVED CALCINATION TECHNIQUE

Superconductor powder synthesis methods that use any species containing carbon are suspect because of the possibility of retaining carbon, especially for products derived from carbonates.¹³ In fact, most bulk processes and even some thin film techniques that use organic precursors¹⁴ have been identified as being highly susceptible to carbon contamination.

The reasons for using a mixture of nitrate and acetate starting materials are related to solubility issues and have been described above. The original calcining process, which involved heat treatment to 825°C in flowing O₂, can lead to carbonate formation. Although powders with very low or nondetectable* carbon content can be prepared by calcining in crucibles in oxygen, scaling up of the process to include rapid calcination in an entrained gas reactor in oxygen or nitrogen led to a dramatic increase in the amount of carbonate formed.

The initial promising results indicated that carbonate-free powders could be prepared if the calcining time, temperature, and atmosphere conditions were controlled. Decomposition of the freeze-dried precursor material during slow calcining in trays or crucibles produces a mixture of NO_x and acetate-derived species during the early stages of calcining. If the amount of precursor is large, and the crucible volume is small, the decomposition products can accumulate and further reactions can occur, depending on the flow rate of the calcining gas and the rate of temperature increase. However, if a large amount of precursor surface is exposed in shallow trays or crucibles, these gases can be removed rapidly and there is little opportunity for reaction with the precursors to form desired species.

An attempt to increase powder production by calcining rapidly in an vertical furnace where the precursor was entrained in a flowing O₂ gas resulted in the formation of a different array of vapor species and the production of powder heavily contaminated with BaCO₃. The time, temperature, gaseous environment, and degree of contact between powder and vapor species are all different in this procedure. Rapid decomposition of acetates at elevated temperatures leads to the formation of CO₂ gas and the subsequent formation of BaCO₃. Carbonates are difficult to remove entirely, and their formation should be avoided if high purity powder is to be synthesized.

* As detected by XPS, courtesy of Stanford University.

Leary et. al.¹⁵ have shown the effects of annealing a YBCO powder prepared by the solid state route in NO₂ at high temperatures (>600°C). This work showed that treatment of starting materials with NO₂ at 600°C-1,000°C produces a substantially single phase homogeneous superconductor. However, there were no previous reports of the use of gases such as NO₂ for calcining at lower temperatures.

We investigated the effects of various calcining gases, including NO₂, on the production of BaCO₃ or any other detectable carbon from mixtures of organic and inorganic precursors to YBCO, with the objective of refining the calcining process such that carbonate-free powders could be synthesized. From the composition of the gaseous products produced during calcining and those produced during the higher sintering temperatures, we postulated possible reactions that occurred as the temperature of the solid freeze-dried precursor was raised. Results of this study showed that modifications to the calcining process were necessary. Foremost among the changes were (1) the addition of gaseous acid vapors that preclude the formation of carbonate and (2) the use of a two-stage calcination procedure.

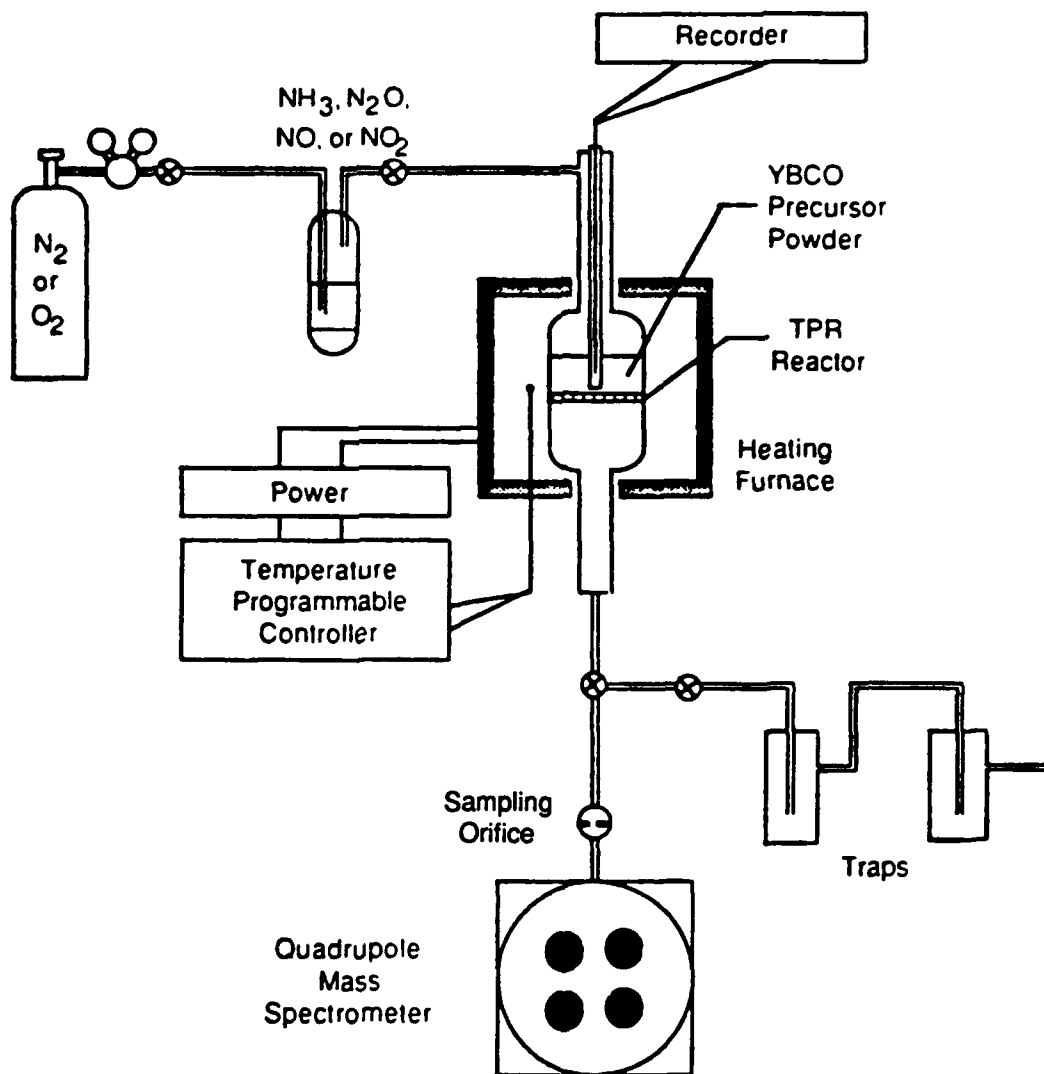
The results of this study point the way to a unique method for handling not only freeze-dried precursors but also other organic-containing material derived from such techniques as coprecipitation, sol-gel, xerogel, and other oxide precursors. The two-stage calcination method described here has been patented.¹⁶

EXPERIMENTAL PROCEDURES

Temperature Programmed Reactor (TPR) Experiments

A 600-g batch of freeze-dried precursor was made using the techniques described above from ~4 liters of 0.13 M solution (with Y as the concentration basis) containing barium acetate and the nitrates of yttrium and copper. All experiments used the same batch of precursor material. Temperature programmed reaction (TPR) experiments were performed using the freeze-dried precursor. The TPR technique is used routinely to characterize the behavior of catalysts. Here it proved useful in determining the composition of the gaseous products evolved during the calcining of the superconductor precursor.

A 0.5-g sample of freeze-dried precursor was loaded into a quartz microreactor under a nitrogen atmosphere, sealed, and transferred to the TPR system (Figure 12). During the TPR experiment, a dilute stream of reactant gas is continuously passed over the sample at a fixed rate. The temperature and heating rate are controlled by a thermocouple attached to the outside of the microreactor. A thermocouple placed inside the reactor bed is used to record the reaction temperature.



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Figure 12. Schematic of temperature programmed reactor (TPR).

The sample was heated from room temperature to 900°C at 10°C/min while the reaction products were analyzed by a quadrupole mass spectrometer and recorded by a data acquisition system.

Reactive gases (calcining gases) added to the inert gas stream included N₂, O₂, NO₂/N₂, NO/N₂, N₂O/N₂, and NH₃/N₂. The gas ion species sampled and recorded by the mass spectrometer are given in Table 12.

Table 12
GAS SPECIES

Chemical Formula	Atomic Mass Units	Chemical Formula	Atomic Mass Units
CH ₄ ⁺	16	N ₂ O ⁺	44
NH ₃ ⁺	17	CH ₃ CHO ⁺	44
H ₂ O ⁺	18	NO ₂ ⁺	46
N ₂ ⁺	28	CHOOH ⁺	46
CO ⁺	28	CH ₃ COCH ₃ ⁺	58
NO ⁺	30	CH ₃ COOH ⁺	60
CH ₂ O ⁺	30	NO ₃ ⁺	62
O ₂ ⁺	32	N ₂ O ₄ ⁺	92
CO ₂ ⁺	44	CH ₃ COOCOCH ₃ ⁺	102

After each TPR experiment, the powder remaining in the quartz microreactor was removed and analyzed by XRD to determine the phase composition and to determine if any BaCO₃ was present. However, small amounts of BaCO₃ cannot be detected by XRD even though these amounts are sufficient to seriously compromise the superconducting behavior. Differential thermal analysis (DTA) is much more sensitive to trace amounts of BaCO₃, and DTA scans were run on samples where XRD indicated no BaCO₃. We used the absence of a decomposition peak as indication of the content of BaCO₃ below 0.1%.

As discussed in a later section, NO₂ was found to be the most effective gas for minimizing or eliminating the carbon contamination and was used in the fluidized bed studies described below.

Fluidized Bed Experiments

The findings of the TPR experiments were incorporated into a new two-stage calcining procedure involving the use of a fluidized bed reactor as the first stage. A vertical furnace was the second stage of this process. A flowchart of the calcination process is shown in Figure 13.

A typical fluidized bed experiment used 25 grams of freeze-dried precursor loaded into a quartz reactor ranging from 3 to 8 cm in diameter, making a bed 3 to 10 cm high. Approximately 5 cm of quartz rashing rings were placed under a quartz frit. The frit both supported the freeze-dried

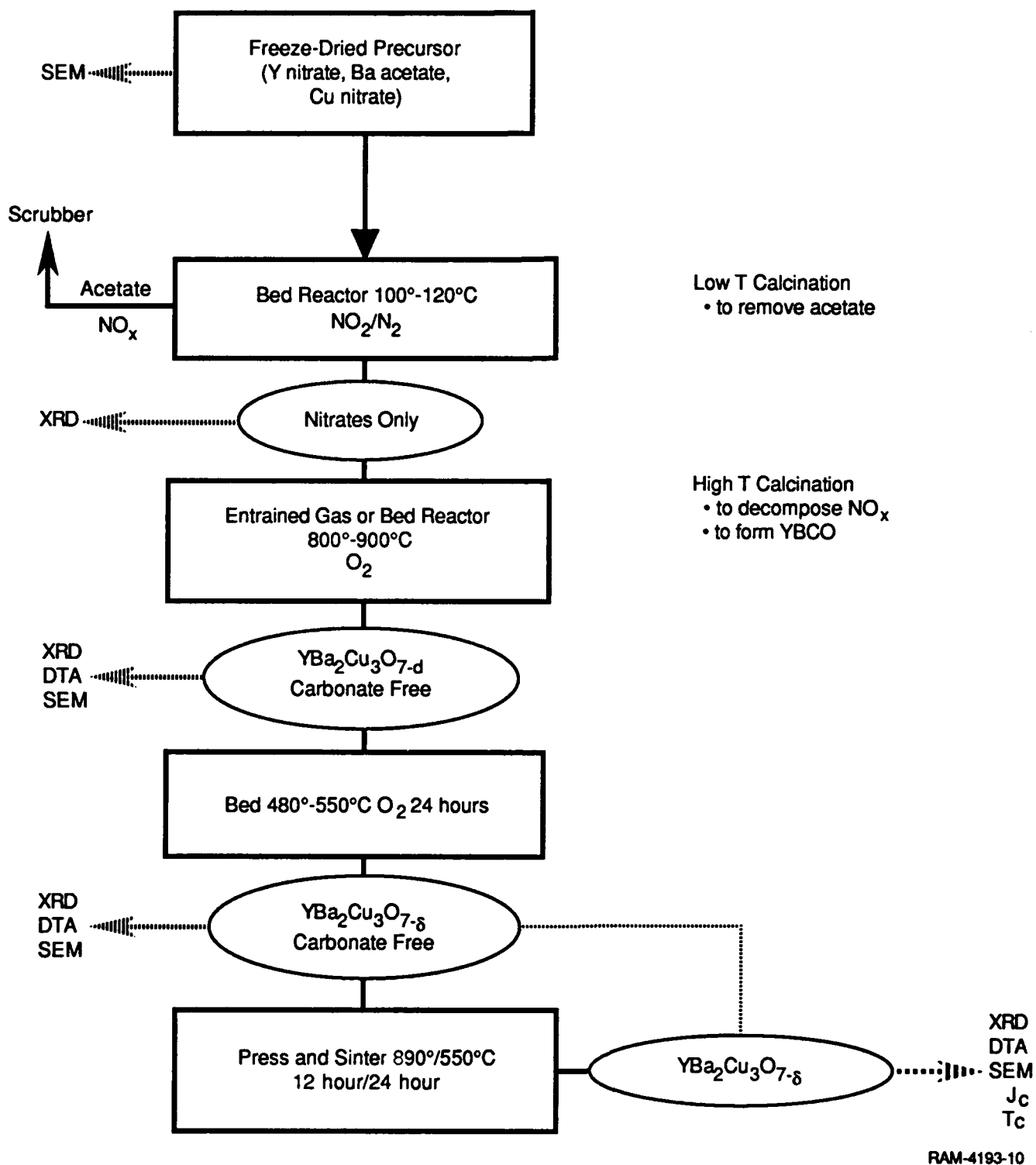


Figure 13. Flowchart of the two-stage calcination process.

precursor powder bed and dispersed the reactant gases. The powder was loaded into the reactor under a nitrogen atmosphere because the precursor is hygroscopic.

The bed was initially fluidized using nitrogen gas, then slowly warmed to between 40°C and 100°C. After the initial warming and fluidization period, nitrogen dioxide gas was slowly introduced into the gas stream via either a NO₂ bubbler or a heated sample cylinder containing liquid NO₂. The concentration of NO₂ in the gas stream was slowly increased until it reached 1%-60%. The temperature of the bed was either maintained at 100°C or slowly raised at ~2°C/min to ~130°C. The bed was kept fluidized under the NO₂/N₂ gas mix for 10-30 minutes at temperature. The reactor was allowed to cool to room temperature while maintaining fluidization of the bed of precursor with the NO₂/N₂ gas.

After the first stage (low temperature) of the calcination process, the powders were treated in one of two ways.

- (1) The prereacted precursor was transferred under N₂ into a warm dry alumina crucible. The crucible was then placed directly into a calcining furnace preheated to 200°-350°C with O₂ flowing at 0.5-1 L/min. The temperature was raised at ~3°C/min to between ~750°-825°C and held at temperature for 3-16 hours.
- (2) The fluidized bed reactor contents were also fed directly into an entrained flow vertical reactor at 900°C with a continuous flow of O₂ calcining gas. In this case, the calcined powder was collected by a system of cyclones and bags.

A flow diagram of the overall powder processing technique from freeze-drying to calcining was shown earlier in Figure 1.

Sintering

The calcined powder was ground in a mortar and pestle and pressed both uniaxially and isostatically into 12-mm-diameter pellets. Uniaxial pressures were 7,000-10,000 psi, while isostatic pressing was done at 70,000 psi. Pellets were then sintered at 890°C for 24 hours and annealed through the 550°-480°C temperature range for 24 hours.

Characterization and Evaluation

XRD was performed after both the low and high temperature calcining steps and on the sintered compacts. DTA was performed on materials after the high temperature/O₂ calcining step and on kerf material from the sintered compacts to assure the absence of BaCO₃. All the DTAs were performed in a flowing oxygen atmosphere with a heating rate of 20°C/min. Further identification of carbon was made using Auger electron spectroscopy (AES) on a sintered pellet.

T_c was measured using a four-point probe, and J_c measurements were made on some of the pellets using a vibrating sample magnetometer.

RESULTS

TPR Experiments

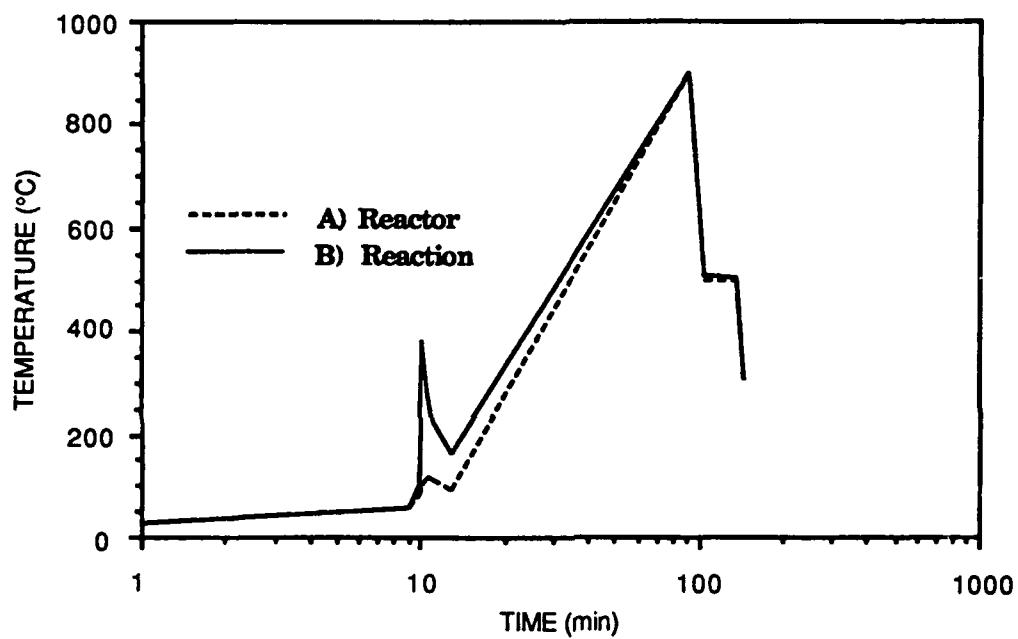
Figure 14 shows the temperature profile of a typical TPR experiment. Heating profile A is the temperature of the exterior surface of the reactor wall, i.e., the controlling thermocouple, and profile B is the temperature of the reaction as measured inside the quartz microreactor.

Figure 15 summarizes TPR experiments performed on the freeze-dried YBCO precursor using the reactant gases listed previously. The figure shows the temperature profile of each run with indications, in some cases, of temperatures at which reactant gases were changed. To the left of each profile is a summary of the phases detected using XRD and the relative strength of each, with peak intensities indicated as very strong (VS) to very weak (VW).

TPR in N_2 and O_2 . Substantial gas evolution was detected between 240°-260°C during TPR experiments using N_2 and O_2 , and brown NO_x was seen at the exit of the gas scrubber. TPR curves for N_2 (Figure 16), and O_2 (Figures 17) are shown. The ordinate indicates peak intensities proportional to partial pressures (in arbitrary units). The drop in partial pressure of N_2 occurs simultaneously with an increase in partial pressures of NO_2 , NO , and O_2 . XRD analyses of the powders indicated the presence of $BaCO_3$.

TPR in NO_2/N_2 . A 25%/75% mixture of NO_2/N_2 was used to explore the possibility of displacing the acetate ligand on the ionic BaO in the freeze-dried material with the nitrate ion. A rapid temperature rise was observed at 150°C (to 250°C). This temperature increase marked the onset of decomposition of (or reaction with) the acetate in the precursor. Only methane, acetone, and water vapor were formed with no nitrogen or carbon oxides observed, Figure 17(a) and (b). The amount of NO_2 in the exit gas decreased during this temperature excursion, indicating consumption or reaction of NO_2 with the precursor to form barium nitrate and displacement of the acetate. The evolution of nitrogen oxides, which signals the decomposition of the nitrates, was finally observed at 250°C. XRD analysis of this calcined powder showed only the YBCO phase and no carbonate. A second identical experiment yielded the same results.

TPR in NO/N_2 . A 50%/50% mixture of NO/N_2 was used for calcination. XRD analysis of this calcined powder showed mostly YBCO phase with a trace amount of barium carbonate.



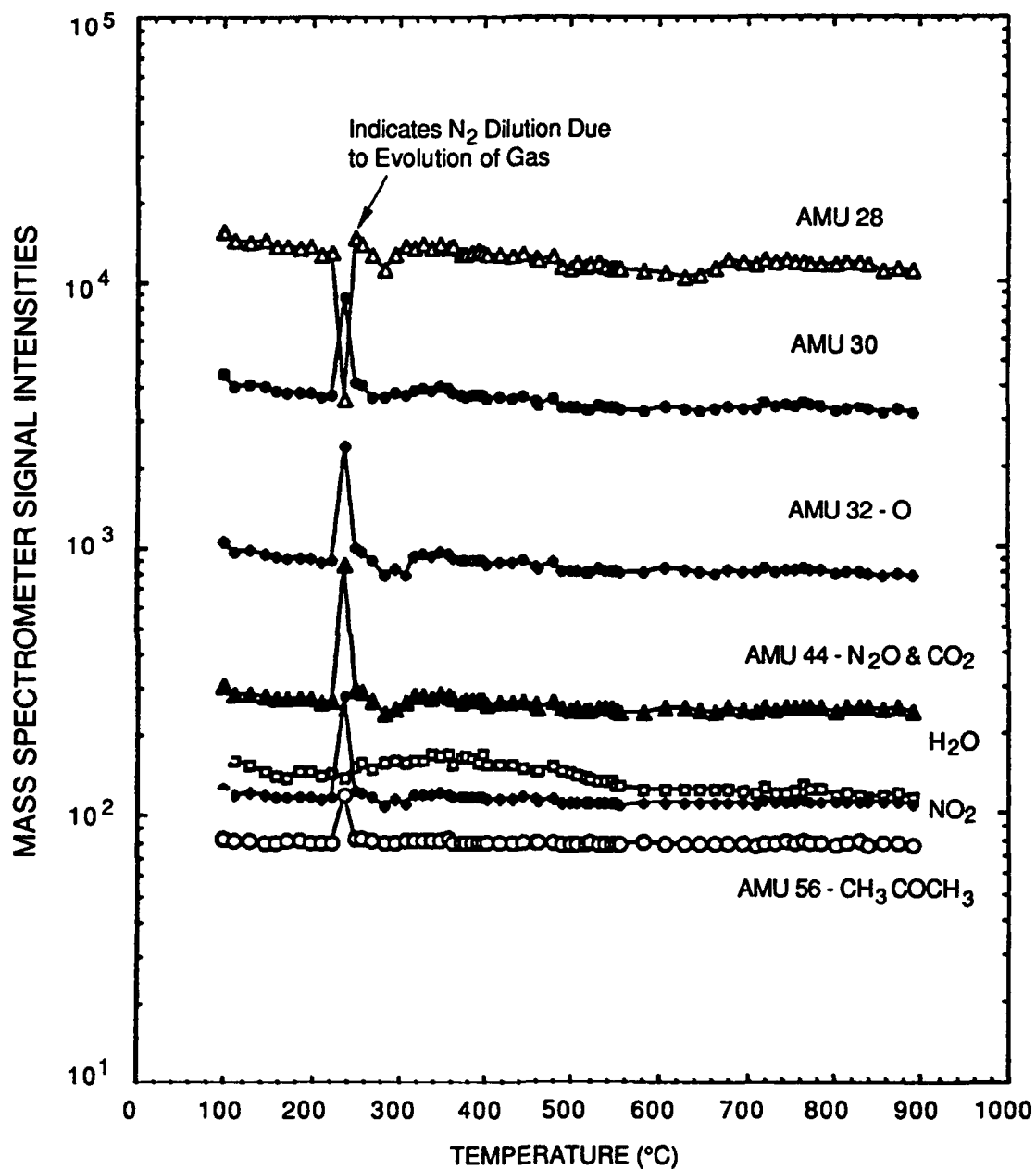
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Figure14. Temperature profile of TPR run 17 showing reactor wall temperature and reaction temperature.

TPR RUN	Reactant Gases & Temperature Profile	YBCO	2-1-1	BaCO ₃	CuO	Y ₂ O ₃	Other
1	N ₂ 100 900 500 100	VS	W	VW	Ø	Ø	M
2	N ₂ 100 900 500 100	VS	W	W	Ø	Ø	S
3	O ₂ 100 900 500 100	VS	VW	S	VW	W	
4	N ₂ O 100 900 500 100	M	Ø	VS	S	Ø	
5	N ₂ /NO ₂ 100 900 500 100	VS	W	Ø	Ø	VW	
6	NH ₃ 100 900 500 100	Ø	Ø	S	Ø	W	VS (Cu)
7	N ₂ /NO ₂ 100 900 500 100	VS	W	Ø	Ø	Ø	S
8	N ₂ /N ₂ O 100 900 500 100	VS	W	VW	VW	Ø	
9	N ₂ /HNO ₃ /H ₂ O 100 625 900 500 100 N ₂ O	VS	W	Ø	Ø	Ø	W (Y ₂ BaO ₄)
10	N ₂ /HNO ₃ /H ₂ O 100 625 900 500 100 N ₂ O	Ø	Ø	Ø	M	Ø	S (Ba(NO ₃) ₂)
11	NO 100 900 500 100	M	Ø	VS	M	Ø	
12	N ₂ 100 325 900 500 100 N ₂ /HNO ₃ /H ₂ O N ₂ O	VS	M	Ø	Ø	Ø	
13	N ₂ 100 325 900 500 100 N ₂ /HNO ₃ /H ₂ O N ₂ O	VS	Ø	Ø	Ø	W	
14	N ₂ 100 325 900 500 100 N ₂ /HNO ₃ /H ₂ O N ₂ O	S	S	Ø	W	Ø	
15	NO 100 650 900 500 100 N ₂ O	Ø	M	Ø	S	Ø	S
16	NO 100 650 900 500 100 O ₂	S	Ø	M	Ø	Ø	VS
17	NO 100 650 900 500 100 O ₂	VS	W	S	Ø	Ø	
18	N ₂ /1%NO ₂ 100 650 900 500 100 HOLD 30min. O ₂	VS	W	Ø	Ø	Ø	

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Figure 15. Phases detected in XRD scans of powders after TPR scans.



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Figure 16. Mass spectrometer signals during TPR of YBCO precursor in N₂ environment at 10°/min up to 900°C.

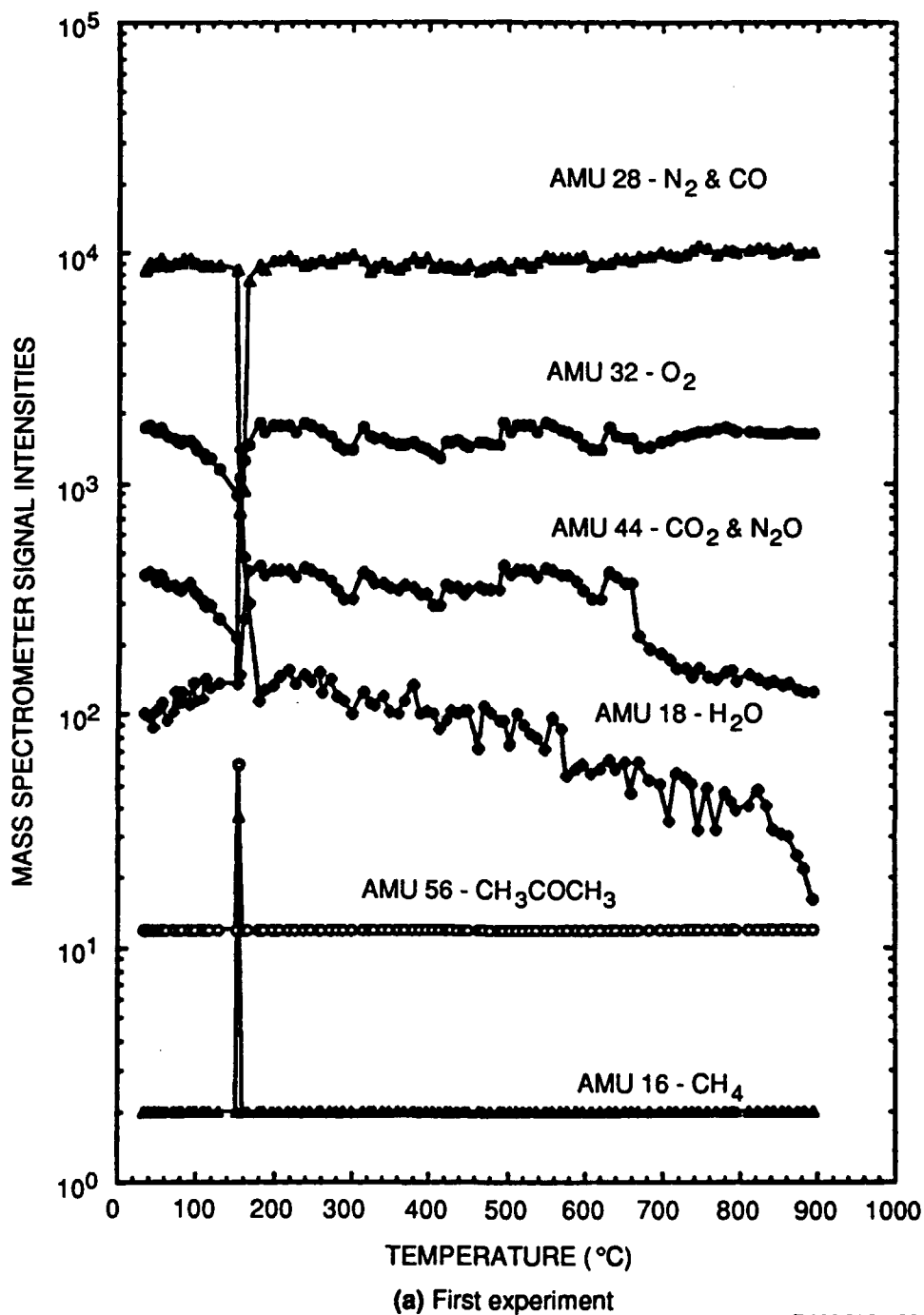
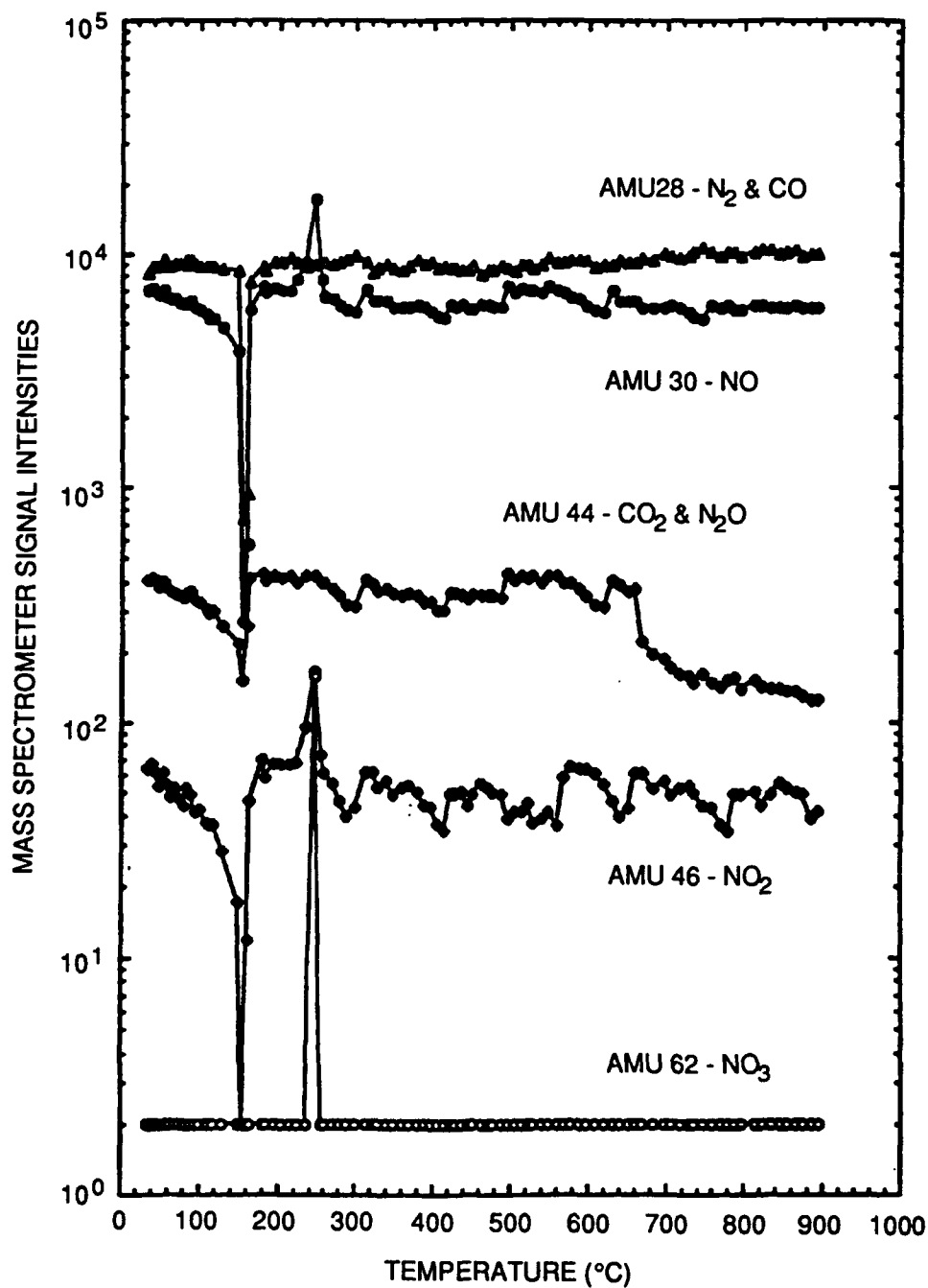


Figure 17. Mass spectrometer signals during TPR of YBCO precursor in NO_2/N_2 environment at 10%/min up to 900°C.



(b) Second experiment

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Figure 17. Mass spectrometer signals during TPR of YBCO precursor in NO_2/N_2 environment at 10%/min up to 900°C. (Concluded)

TPR in $\text{N}_2\text{O}/\text{N}_2$. A 50%/50% mixture of $\text{N}_2\text{O}/\text{N}_2$ was used for calcination because, unlike NO_2 , N_2O is not poisonous. A similar temperature rise to 290°C at 190°C was observed with simultaneous evolution of methane, nitrogen and carbon oxides, acetone, and water vapor. A second evolution of these gases except methane and water vapor was again observed at about 250°C , signaling the complete decomposition of the remaining nitrates and acetate. XRD analysis of this calcined powder showed BaCO_3 in the final YBCO phase.

TPR in NH_3/N_2 . A 25%/75% mixture of NH_3/N_2 was used to explore the effects of a basic/reducing environment on calcination. There was a rapid temperature rise at 250°C (to 410°C), signaling an onset of reaction of the precursors. XRD analysis of this calcined powder showed that metallic Cu, Y_2O_3 , and BaCO_3 formed, suggesting that NH_3 is too strongly reducing and not suitable for calcining.

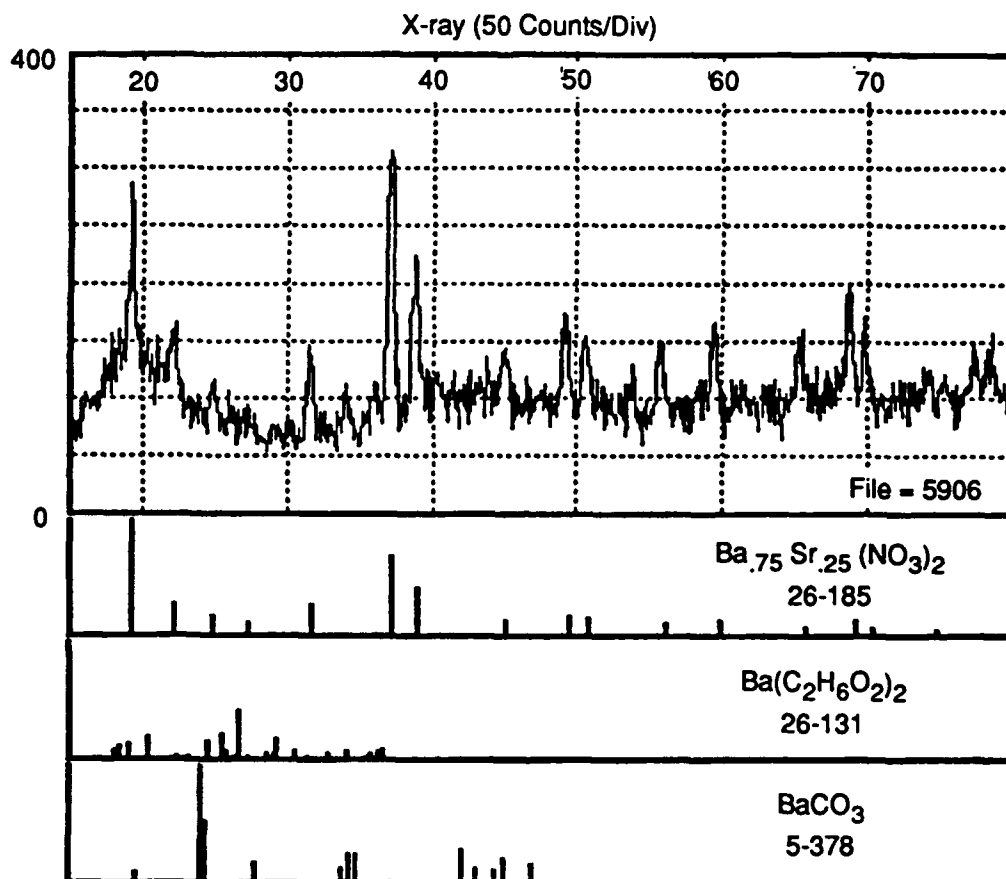
Fluidized Bed Experiments

XRD Results. The temperature during the first stage of the calcination (fluidized bed calcination) must be maintained below $\sim 145^\circ\text{C}$ because an explosive reaction that occurs at that temperature leads to oxidation and formation of large quantities of copper oxide. The powder forms hard agglomerates if this reaction occurs.

However, if the temperature is maintained below 145°C , the product is a Ba-Y-Cu- NO_3 phase. XRD of the NO_2/N_2 prereacted precursor indicated that the major phase present had a structure that correlated exactly with the structure for $\text{Ba}_{0.75}\text{Sr}_{0.25}(\text{NO}_3)_2$ (PDF 26-185) (Figure 18), leading to the reasonable assumption that the actual major phase present was a Ba-Y-Cu compound of the same structure. More important, no BaCO_3 or $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ was detected in the product.

XRD of NO_2/N_2 prereacted material calcined in alumina crucibles in an O_2 flow showed no carbonates present in the material calcined for 3 hours at 770°C or at 825°C . XRD of kerf material from sintered/annealed pellets also showed no carbonates (Figure 19).

DTA Results. The DTA traces from calcined and sintered materials made from prereacted precursor showed no evidence of BaCO_3 . Thermal events were compared with data from Aselage and Keefer¹⁷ and with oxygen atmosphere endotherm temperatures reported by J. E. Ullman et. al.¹⁸ Transitions in crystal structure in BaCO_3 are given in Table 13.¹⁹



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Figure 18. X-ray diffraction pattern of freeze-dried precursor after prereacting in fluidized bed with NO_2/N_2 gas mix at 110°C for ~20 min.

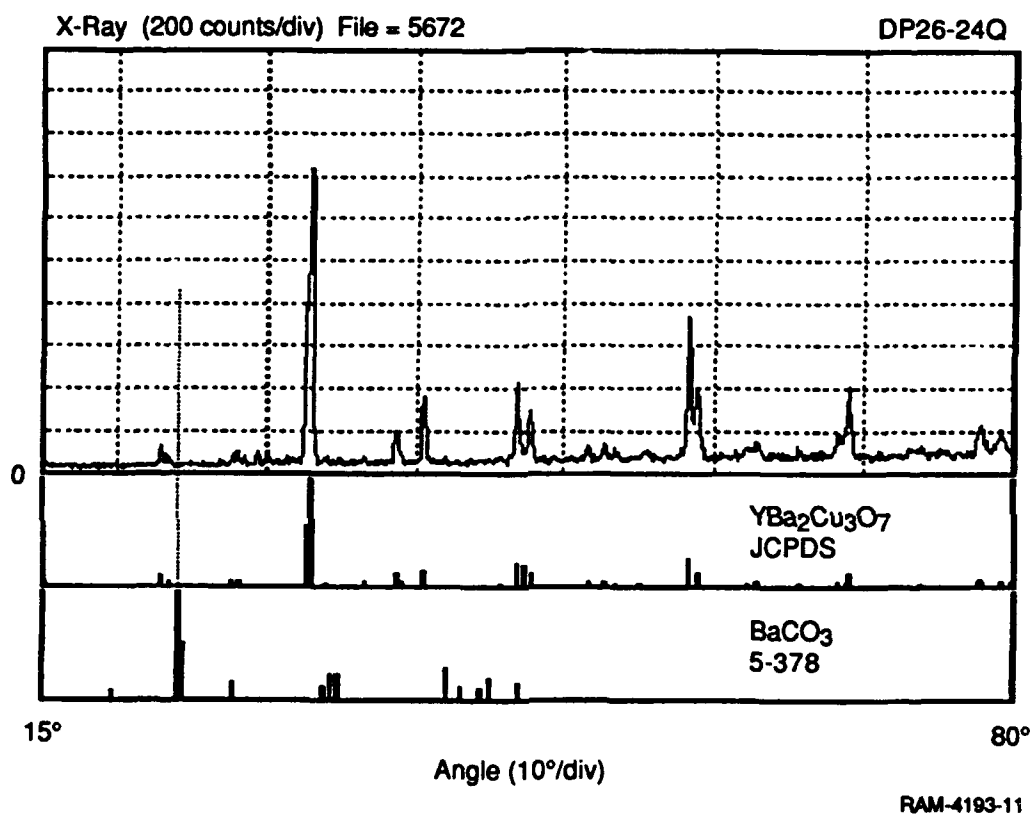


Figure 19. XRD pattern of YBaCu₃O_{7.8} powder without BaCO₃ (ground from sintered material).

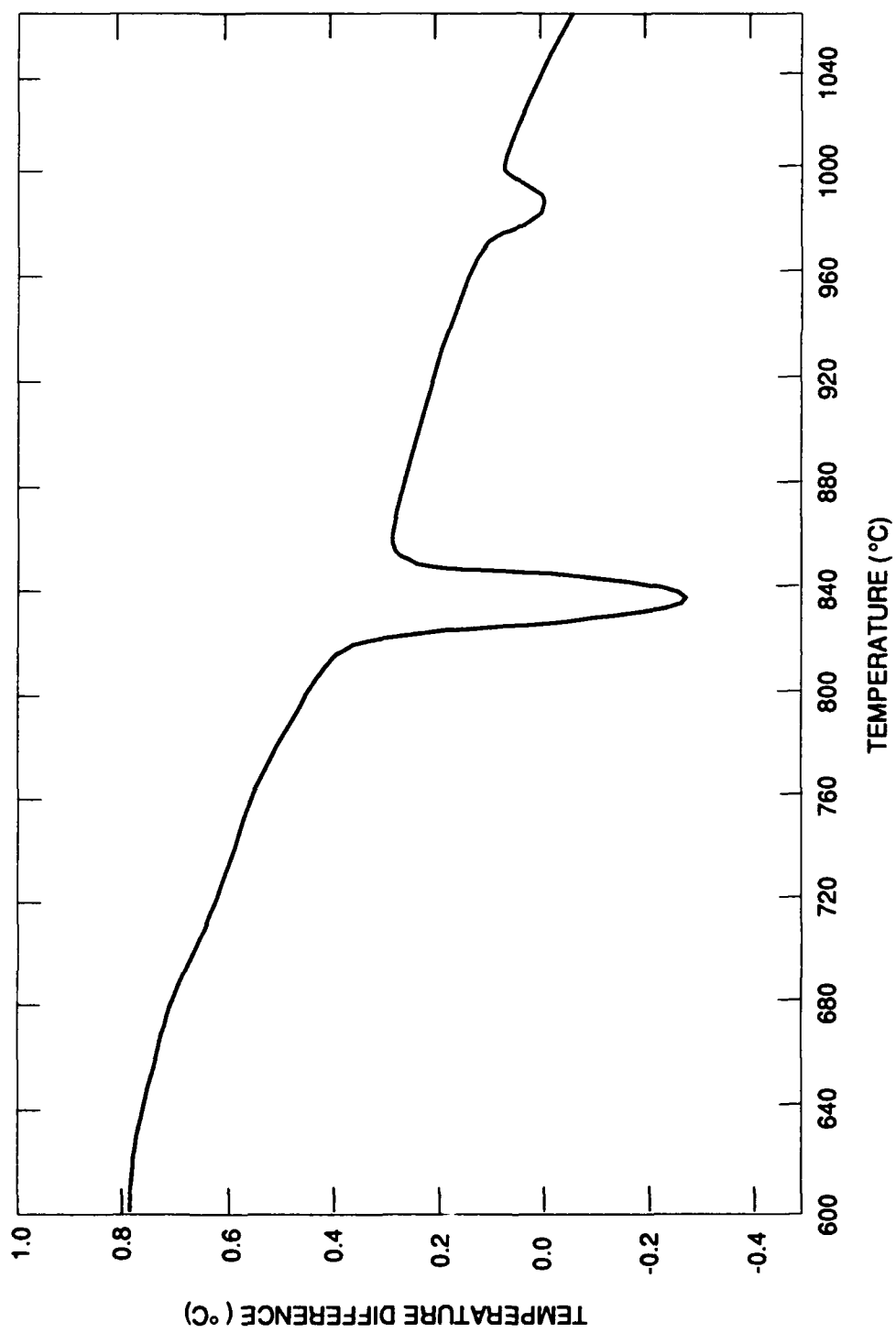
Table 13
BARIUM CARBONATE TRANSITIONS

<u>Crystal Structure</u>	<u>Temperature Range (°C)</u>	<u>Enthalpy of Transition (kcal/mole)</u>
Orthorhombic	to 806	+4.5
Hexagonal	to 968	+ 0.7
Cubic	to decomposition	

For comparison, DTA under O₂ was performed on a 99.9% pure BaCO₃ sample (Figure 20). Endotherms at 821°C and 974°C coincide with the γ -to- β and the β -to- α transitions, respectively. Typical DTA results are shown (Figure 21) for a 12-mm-diameter compact isostatically pressed at 70,000 psi. No correlation was found with any of the thermal events reported for BaCO₃.

Auger Results. Although the XRD and DTA results indicated that there was no BaCO₃ present, the detection levels for these techniques still leave some questions. The detection limit for DTA, the best of these methods, is < 0.5 wt/%. Auger electron spectroscopy (AES) was used to confirm the absence of C (Figure 22). AES was performed on a sintered pellet that received no special handling other than to be placed by hand into a plastic container. Six measurements were made, starting at the surface and measuring at 1-minute intervals during sputtering down to 60 Å below the surface. Surface carbon was evident (at an atom fraction of 0.17), as might be expected from a sample that was exposed to air and handling. However, no carbon was detected after etching for 1 min with Ar⁺ at a rate of 12 Å/min. No carbon was detected in any of the subsurface measurements.

T_c and J_c Results. T_c measurements were made using a 100-μV criteria and gave sharp transitions at 90-91K with transition widths, ΔT (defined by the temperature between the 90% of the normal state resistivity near T_c and the temperature at zero resistivity) of ~1-2K. There was no broadening of the curve when isostatically pressed samples were compared with uniaxially pressed samples. A temperature/resistivity curve for Sample FBR-6a is shown in Figure 23.



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Figure 20. DTA scan of pure BaCO_3 .

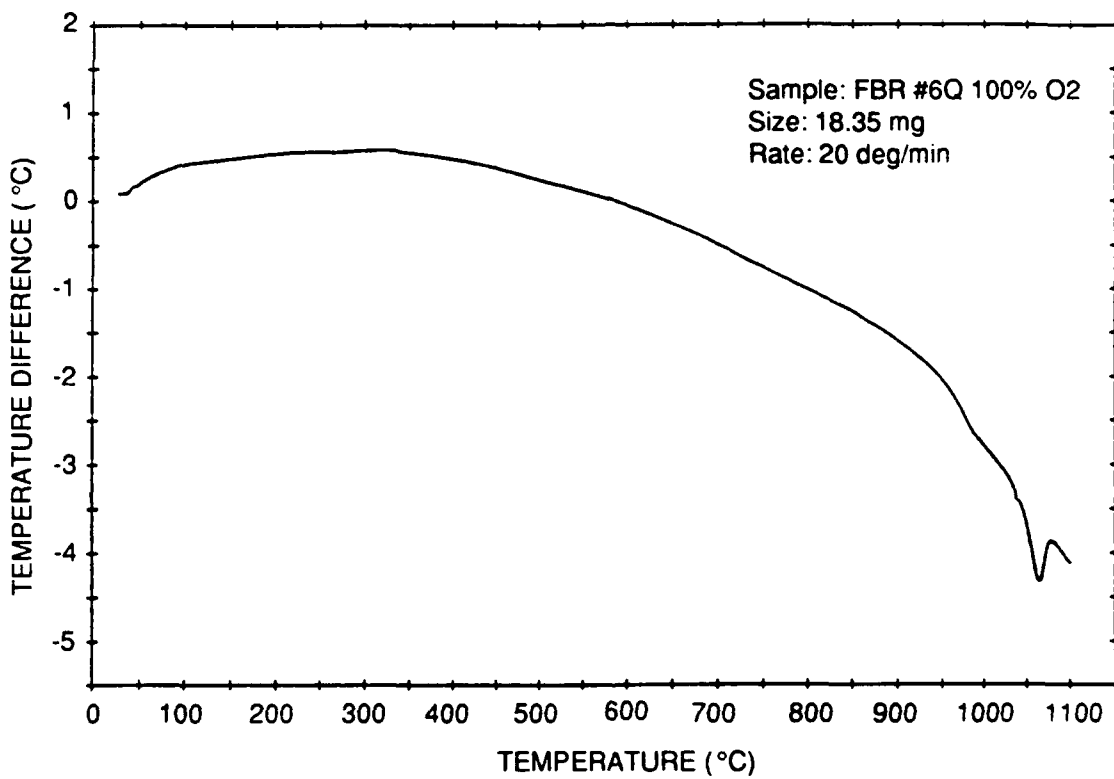
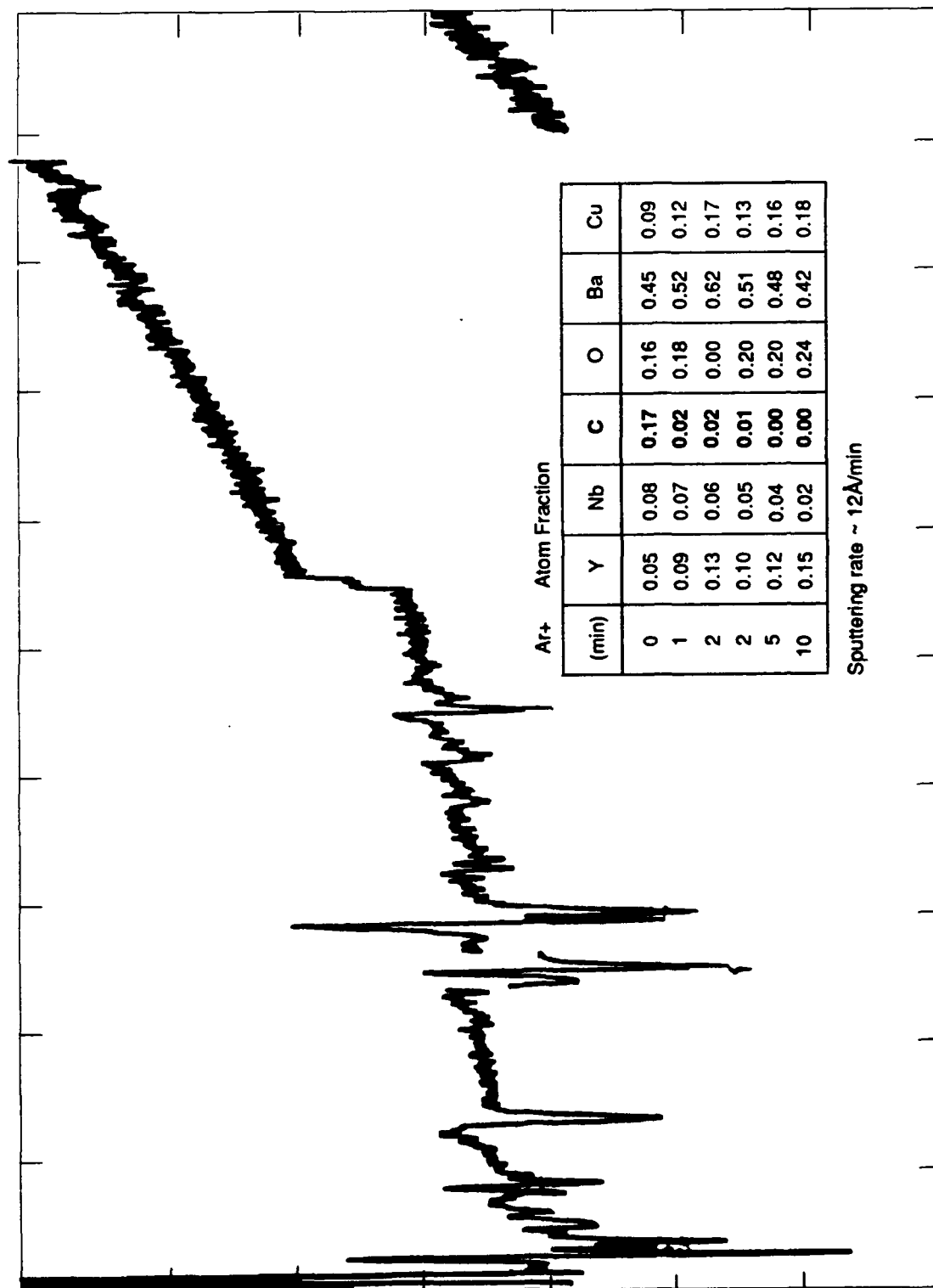


Figure 21. DTA scan of carbonate-free YBCO powder.



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Figure 22. Auger scan of sintered sample made from carbonate-free powder (sample FBR-6Q).

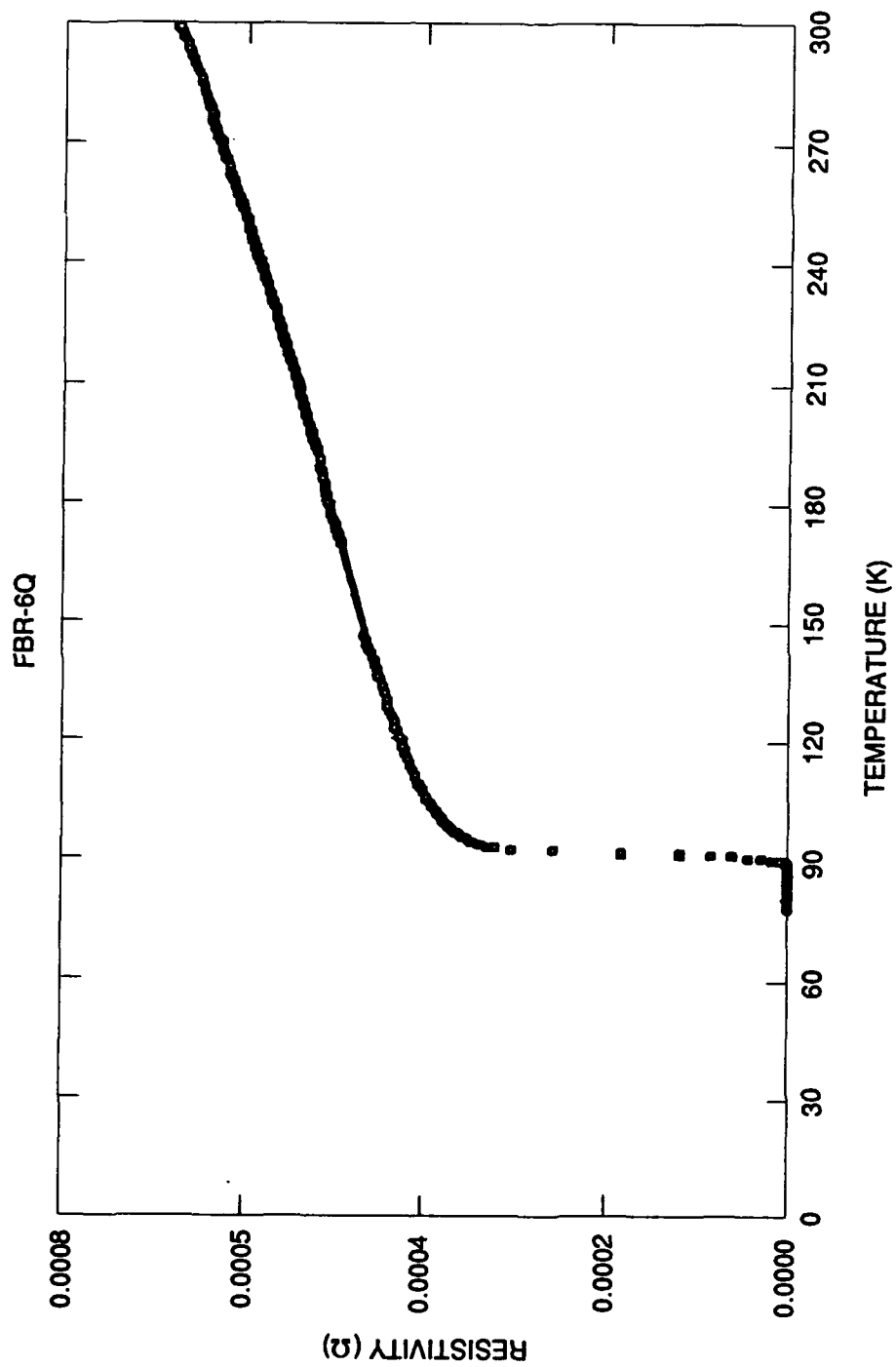


Figure 23. Temperature resistivity curve of sintered sample made from carbonate-free powder (sample FBR-6Q).

Critical currents were determined from magnetization measurements (M vs. H) at 5K in a 0.5 Tesla field. These magnetically derived data have shown close agreement with the direct transport measurements of J_c values.²⁰ Table 14 compares the J_c values derived from the new two-step calcining with those from the earlier one-step procedure. This list does not cover all J_c measurements made, but is for comparison only. This comparison shows that the two-stage calcination process improves J_c of the sintered materials dramatically. These results were obtained from a nonoptimized process, and improvements are possible.

Table 14
EFFECT OF TWO-STAGE CALCINATION ON J_c

Sample	Composition	Sinter Temp. (max°C/hrs.)	Critical Current (A/cm ² , 0.5 T)	Comments*
I02	YBCO	890/12	700	SS; Uniaxially
212	YBCO	890/24	2,900	SS; Uniaxially
227	YBCO+Ag	890/24	5,900	SS; Uniaxially
232	YBCO	890/24	6,000	SS; Uniaxially
238	YBCO	950/6	1,600	SS; Uniaxially
FBR-6Q	YBCO	890/24	7,250	DS; Uniaxially
FBR-7Q	YBCO	890/24	14,440	DS; Uniaxially
FBR-8Q	YBCO	890/24	4,500	DS; Isostatically

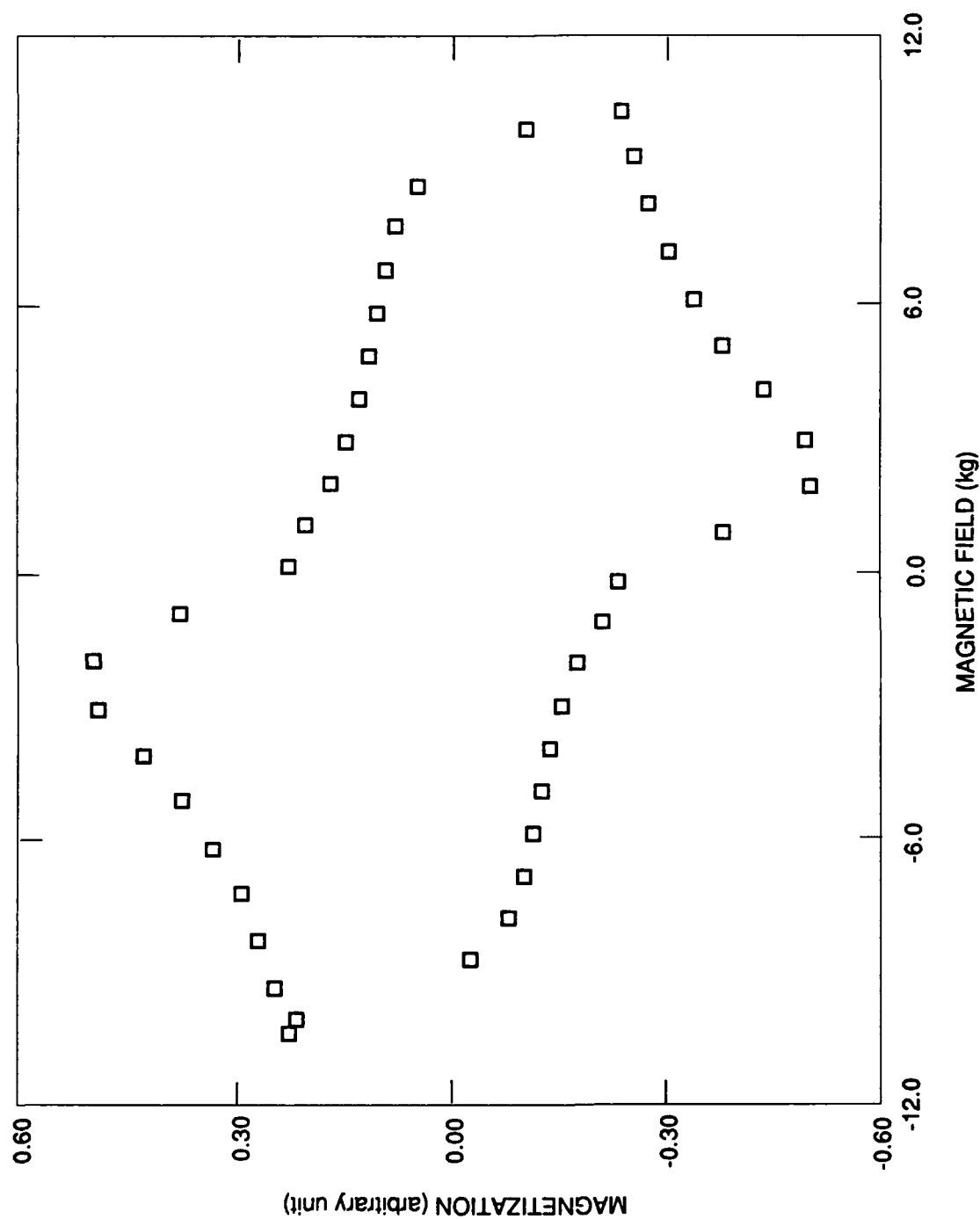
* SS indicates single-stage calcining; DS indicates two-stage calcining; isostatically and uniaxially refer to cold pressing techniques.

Magnetization curves for samples FBR-7Q (uniaxially pressed) and FBR-8Q (isopressed) are shown in Figures 24 and 25. The uniaxially pressed sample has a larger hysteresis loop, as indicated by the higher critical current density.

Microstructure. The density of the samples (~ 85%) was calculated using dimensional data. The density of cold isostatically pressed samples was only ~4%-6% greater than that of uniaxially pressed samples. The powder calcined in the crucible coarsened during the second stage of calcination and was not ground excessively after calcination to avoid contamination from the atmosphere. SEM photos show that the porosity is similar for both pressing methods (Figure 26). Powder processed in the vertical reactor is much finer, but substantial numbers of samples have not been made from this material.

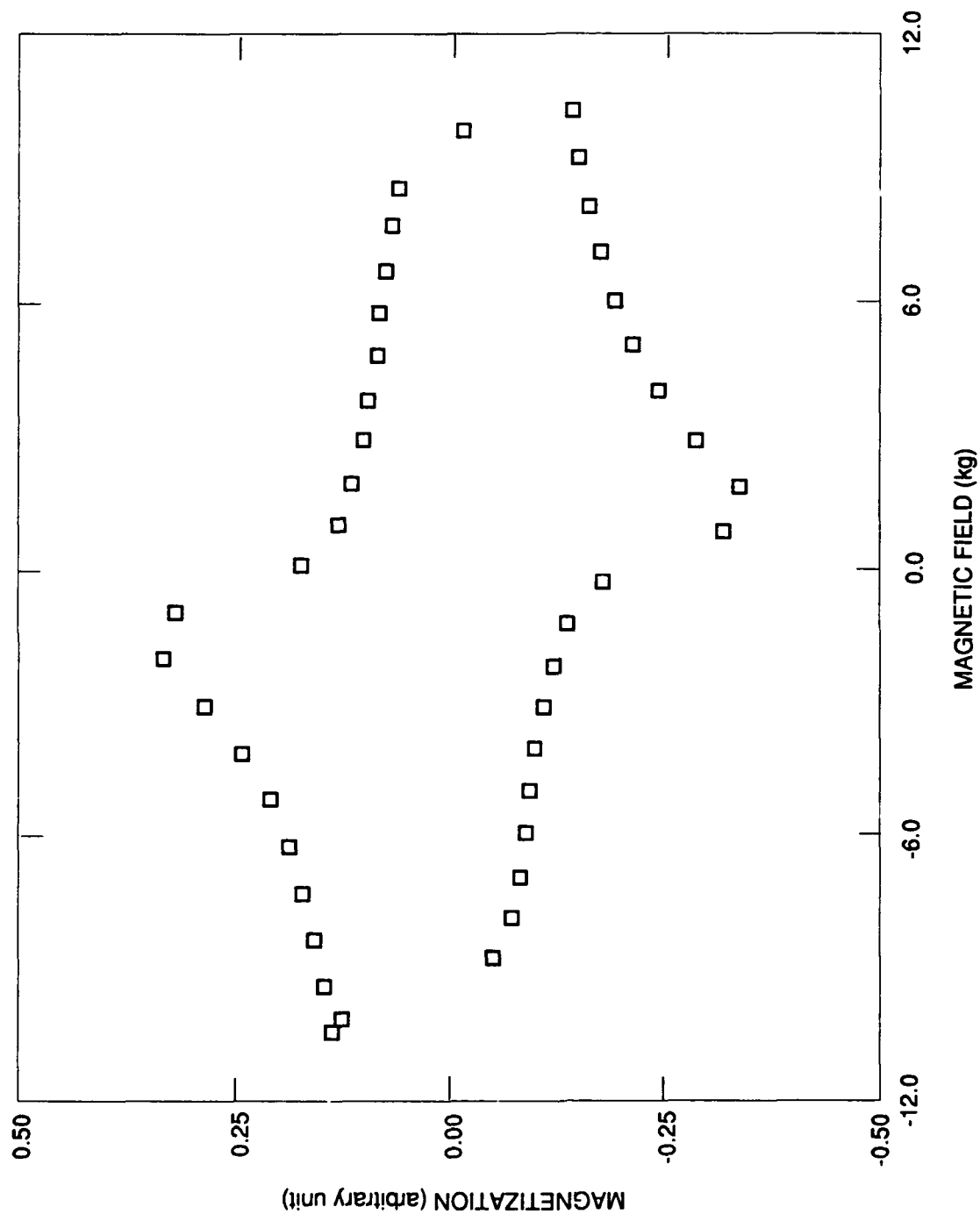
DISCUSSION

The results of this study led to the development of an improved two-stage calcination procedure: a low temperature step in NO₂ and a high temperature step in O₂. The rationale for this calcination process is discussed below.



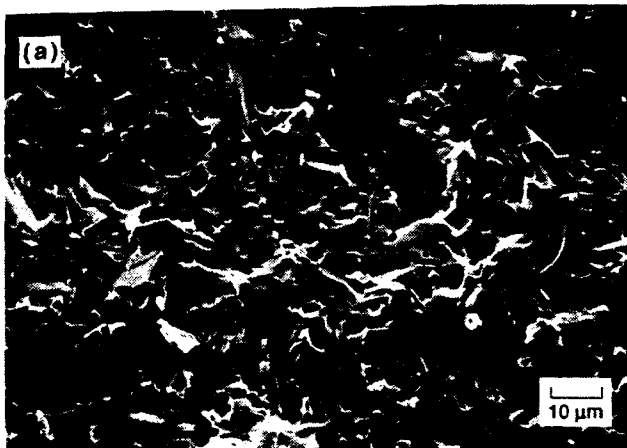
RAM-6585-39

Figure 24. Magnetization curve for uniaxially pressed sintered sample made from carbonate-free powder (sample FBR-7Q).



RAM-6585-40

Figure 25. Magnetization curve for isopressed sintered sample made from carbonate-free powder (sample FBR-8Q).



RPM-6585-23

Figure 26. Microstructure of sintered samples made from carbonate-free powder(sample FBR-8Q). Pellets ramped from 25° to → 890°C in a 1% NO₂/N₂ gas mixture switched to O₂ at 890°C for 24 hr and annealed at 550°C for 24 hr.

a, b: Uniaxially pressed at 10,000 psi
c, d: Isostatically pressed at 70,000 psi

TPR Experiments. The TPR results provided the insight into the chemical reactions occurring during calcination of these mixed nitrate-acetate precursors to YBCO. An exothermic reaction occurs at 220°C when the freeze-dried precursor is treated in N₂ and O₂. We postulate that the decomposition of Ba(COOCH₃)₂ forms CH₃COCH₃ and BaCO₃ at this temperature, based on the presence of CH₃COCH₃ in the gas phase, as determined by mass spectrometry, and BaCO₃ in the final YBCO phase, as determined by XRD. The exothermic temperature rise triggers the simultaneous decomposition of the nitrates and acetate from the precursor in both a N₂ and O₂ environment, leaving BaCO₃ in the final YBCO phase. Ba acetate was treated under flowing N₂ to 600°C to confirm the occurrence of this reaction. The resultant product was BaCO₃.

A second exothermic temperature rise of as much as 200°C is observed when O₂ is introduced at a higher temperature (800°-900°C) in TPR runs where N₂ is used initially as the reactive gas. The temperature rise is probably due to the oxidation of residual carbon left from the decomposition of Ba(COOCH₃)₂ to form CH₃COCH₃ and BaCO₃. CH₃COCH₃ further decomposes to form CH₄, carbon oxides, and deposits of carbon. In the case of the TPR run where O₂ is used as the reactive gas from the beginning, there is no exothermic temperature rise at higher temperature, presumably because the oxidation of residual carbon is continuous.

An exothermic reaction occurred at lower temperatures (150°C) when a NO₂/N₂ mixture was used as the reactive gas. The simultaneous evolution of CH₃COCH₃ and CH₄ and consumption of NO₂ coupled with NO and O₂ seems to support our hypothesis that the acetate associated with Ba(COOCH₃)₂ is displaced by NO₂ to form Ba(NO₃)₂ rather than decomposing to form BaCO₃. It seems that, without this replacement reaction at the low temperatures, BaCO₃ will form and remain in the final YBCO phase. Although large amounts of NO_x will be produced by decomposition of the nitrates in a N₂ or O₂ atmosphere, this occurs at a higher temperature. In this case BaCO₃ has already formed from the decomposition of the acetate and cannot be entirely removed. It is therefore necessary to have an NO₂ atmosphere at lower temperatures to ensure replacement and removal of the acetate anion.

This observation led to the development of a two-stage calcination process in which the first stage consists of a fluidized bed where the precursor is exposed to NO₂ at a temperature below 145°C to remove the acetate, and the second stage consists of calcination in O₂ to decompose the nitrates and form the superconducting phase.

Calcination and Sintering. Fluidized bed experiments were performed to ascertain the most appropriate conditions for performing the first stage of the calcination process for synthesizing carbonate-free superconductor powders. The fluidized bed reactor was chosen as the means of

adding acid vapors such as NO_2 to the gas stream and maintain constant temperature and composition of the gas phase. The hypothesis was that an acidic specie such as NO_2 would displace the acetate from its bond with the basic BaO . By removing the organic ligand at low temperature, and not allowing it to decompose and react to form BaCO_3 , we believed that the formation of carbonate during calcining would be avoided. A fluidized bed was selected as the best method of exposing all the powder to the NO_2 in a reasonable time. Heat treatment times of <1 hour were found to be sufficient for the amount of powder used in these studies.

Two approaches to the second calcination step were taken. In the first, the powder from the low temperature treatment was heat treated in crucibles. In the second approach the powder was fed directly into a vertical free space reactor. The results presented here are for powders treated at high temperatures in crucibles. It was not possible to engineer the vertical reactor as part of this work. The furnaces available were not powerful enough to heat the powder/gas stream to a high enough temperature.

XRD results show no carbonates in either the calcined materials or the sintered materials. Note that the material calcined at 825°C and simply allowed to cool with the furnace power turned off gave an XRD scan of essentially the same quality as that of the sintered and annealed pellet. This similarity indicates that a highly reactive, essentially clean YBCO powder may be formed at considerably lower temperatures than usually reported.

Differential thermal analysis was performed to confirm the absence of BaCO_3 . No correlation to any previously reported BaCO_3 endotherms was observed. However, the presence of liquid from lower temperature reactions could cause variations in event onset temperatures. In previous sintering studies, we showed that material made using the freeze-dried technique appears to be more reactive and that the DTA endotherms may be offset from values reported by others.

Auger electron spectroscopy was used to confirm the results. The AES scan area was $\sim 50\mu\text{m}$, which was enough to encompass several grain boundaries. Optical micrographs and SEM had shown the grain size to be $\sim 10\text{-}30\mu\text{m}$. AES showed no carbon from $12\text{-}60\text{ \AA}$ below the surface of the sample. The detection limit for Auger is 0.1% of the surface population.

The T_c and J_c results indicate that the two-stage process produces an improved powder, even at this early stage of development. Although not conclusive, the lack of broadening in the T_c curves when isostatically pressed samples are compared with uniaxially pressed samples suggests clean, low-carbon samples. However, comparison of J_c values should be more conclusive. If carbon retention is a major contributor to the degradation of superconducting properties of dense

materials as explained by Shaw et al.,¹² then an isostatically pressed sample made from calcined material lacking any carbon should show little or no difference from a less dense uniaxially pressed sample, provided that oxygenation was not a problem.

The two pressing methods were used to explore this point. The results indicate that the J_c is lower for the isopressed sample (Table 14, samples FBR-6Q and FBR-7Q vs. FBR-8Q). However, the characteristics of the powders used in this experiment were far from ideal in terms of size and agglomeration. Critical current densities will improve with improvement in sample densities from the current 85% dense range of this simple crucible calcining method. Even with this preliminary calcining technique, the J_c values are considerably improved over earlier samples.

SUMMARY

The temperature-programmed reaction (TPR) technique was used to characterize the reaction products produced on decomposition of a freeze-dried precursor to YBCO in various calcining atmospheres. We found that the acidic vapors of NO_2 had the most beneficial effect on the YBCO end product, producing a powder that is carbonate-free. Calcination in N_2 , O_2 , and N_2O led to the formation of BaCO_3 .

The above results were used to design a two-stage calcination process for mixed acetate-nitrate precursors to YBCO. The process consists of a low temperature step in a fluidized bed under NO_2 gas and a high temperature step under an O_2 atmosphere. The powders produced by this calcination process have no BaCO_3 present as shown by XRD, DTA, and AES. Pellets sintered from these nonoptimized powders have sharp T_c transitions and the J_c is twice that for previous powders. The best J_c obtained was $14,400\text{A}/\text{cm}^2$ at 0.5 T and 5K.

Further refinement of the calcination process should lead to further improvements in superconducting properties.

CONCLUSIONS

The freeze-drying route to the synthesis of superconducting powders of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ composition was investigated and developed. The basic process was patented during the project, and an improvement in the process was patented at the conclusion of the project. Copies of these patents are given in Appendix B.

Freeze-drying can be used to prepare $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders from a mixture of nitrates and acetates. Synthesis of high quality powders requires understanding and control of the chemistry at all stages. Important variables in the solution preparation include solution concentration and pH. Control of solution composition is crucial for obtaining the desired stoichiometry. Volumetric analysis techniques and a solution preparation protocol were developed as part of this program. Spraying, milling, and drying control the powder characteristics as well as affecting the composition. High surface areas can be obtained by milling the powders after drying and by controlling the calcination conditions. Contamination with carbon, in the form of BaCO_3 is acknowledged as a cause of low critical current density in YBCO superconductors. Initial attempts to scale-up the process resulted in significant BaCO_3 contamination.

A detailed study of the decomposition reactions occurring in the nitrate-acetate mixture led to the development of a two-stage calcination process. In the first, low temperature stage ($<145^\circ\text{C}$) the powder is treated in NO_2 . The acetate ligand is replaced by the more acidic nitrate. The acetate is removed in the gas stream and reaction with BaO is prevented. The second stage consists of a high temperature decomposition of what is now only a mixture of nitrates. The second stage is performed in an O_2 atmosphere. The powder can be calcined either in crucibles or in a continuous flowthrough reactor. The powders described here were calcined in crucibles. Insufficient time was available to develop the large flowthrough reactor, although a preliminary system was assembled.

The major result of the new calcination process was the elimination of carbonate contamination from the powders and a consequent doubling of the critical current density in the first compacts made from the improved powder. The best J_c achieved was $14,400\text{A}/\text{cm}^2$ at 5K and 0.5 T. However, these powders were not optimized in terms of size and final calcining conditions, sintering conditions, or microstructure. Substantial improvements in the calcination process and in the powder and material properties are possible.

Freeze-drying of nitrate-acetate solutions followed by two-stage calcination is thus an effective way of producing high quality superconductor powders. All steps of the process are amenable to scale-up, and the process is potentially economic.

The original freeze-drying technique and the improvement in the calcination technique were patented during this program.

Note: The nitrate-acetate mixtures used in this program can explode on heating.

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APPENDIX A
TITRATION PROCEDURES

DETERMINATION OF Y (BACK TITRATION)

INDICATOR: ERIOCHROME BLACK T

Procedure

- (1) A known quantity of Y nitrate.
- (2) Dilute with distilled H₂O.
- (3) Add excess buffer solution (solution becomes turbid).
- (4) Add excess amount of EDTA.
- (5) Add MeOH to give a 50% solution.
- (6) Add 10 drops of indicator.
- (7) Titrate with standard MgSO₄.
- (8) Color change from blue to pink.

Source: Frank J. Welcher, (D. Van Nostrand Company Inc., Princeton, NJ 1958). *The Analytical Uses of Ethylenediamine Tetraacetic Acid*.

DETERMINATION OF Ba

Procedure:

- (1) Weigh 0.5 g Ba acetate and add 50 mL of distilled H₂O in a 400-mL beaker.
- (2) Add 1 mL of concentrated HCl.
- (3) Dilute to ~200-mL solution.
- (4) Heat the sample just to boiling.
- (5) Add ~25 mL, 0.25 m (NH₄)₂SO₄ solution dropwise (this includes an excess) and stir constantly.
- (6) Let the precipitate settle, no more stirring, cover the beaker with a watch glass, and keep temperature at ~60°C (hot) for more than 1 hr.
- (7) Wash crucible that will receive the precipitate.
- (8) Support the crucible, without cover, on a triangle and heat to redness for 10 min.
- (9) Let cool in air for a few minutes until only moderate radiated heat is felt.
- (10) Put the crucible in a desiccator for more than 30 min until it cools completely.
- (11) Weigh crucible accurately.
- (12) At the end of digestion period, again test for complete precipitation by adding a few drops of (NH₄)₂SO₄ solution down the side of the beaker.
- (13) Filter the solution, disturbing the precipitate as little as possible.
- (14) Rinse the beaker and bring the precipitate onto the filter paper.
- (15) Fold the filter paper from the four corners and put into the weighed crucible.
- (16) Support the uncovered crucible on a triangle well above a small flame and heat gently so that the paper dries before beginning to char.
- (17) Gradually raise the temperature to char the paper avoiding active combustion with a flame. Burn off all the carbon.
- (18) When the residue in the crucible is white or nearly so, heat the inclined crucible at full burner temperature for 10 minutes.
- (19) Cool for more than 30 min and weigh accurately.

APPENDIX B
PATENTS ON FREEZE-DRYING PROCESSES

United States Patent [19]

Gusman et al.

[11] Patent Number: 4,975,415

[45] Date of Patent: Dec. 4, 1990

[54] CRYOCHEMICAL METHOD OF PREPARING ULTRAFINE PARTICLES OF HIGH-PURITY SUPERCONDUCTING OXIDES

[75] Inventors: Michael I. Gusman, Palo Alto; Sylvia M. Johnson, Piedmont, both of Calif.

[73] Assignee: SRI - International, Menlo Park, Calif.

[21] Appl. No.: 71,977

[22] Filed: Jul. 10, 1987

[51] Int. Cl.⁵ C01F 17/00; C01G 3/02

[52] U.S. Cl. 505/1; 505/730; 505/737; 505/738; 505/742; 264/12; 423/263; 423/593; 423/604

[58] Field of Search 264/12; 505/1; 423/263, 423/593, 604; 252/521; 505/730, 734, 738, 742

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(List continued on next page.)

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Attorney, Agent, or Firm—Phillips, Moore, Lempio & Finley

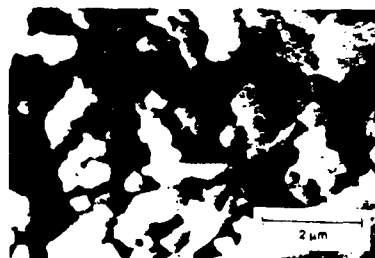
[57] ABSTRACT

The present invention pertains to a method of preparing particles of superconducting ceramic powders, which method comprises:

- (a) dissolving the soluble salts of the cations in aqueous medium;
- (b) obtaining a solution having pH of between about 4 and 7 by optionally treating the aqueous medium with ammonia, or ammonium hydroxide;
- (c) atomizing the solution of step (b) onto liquid nitrogen at about -196° C.;
- (d) removing the liquid nitrogen by evaporation;
- (e) removing the water by sublimation at reduced pressure;
- (f) heating the solid residue of step (e) at 40-60° C. at reduced pressure;
- (g) calcining the solid residue in flowing oxygen or air at temperature of between about 200° to 895° C.; and
- (h) cooling the solid at a temperature of between about 900° C. and ambient temperature in sufficient air or oxygen and recovering the superconducting powder having an average diameter of between about 0.1 and 10 microns.

Optionally, substep (h), additionally includes during cooling, the annealing of the particles in sufficient oxygen at between about 200° and 500° C. for between about 2 and 30 hrs. YBa₂Cu₃O_{7-d} (where d is 0-1) is preferred superconducting powder.

26 Claims, 4 Drawing Sheets



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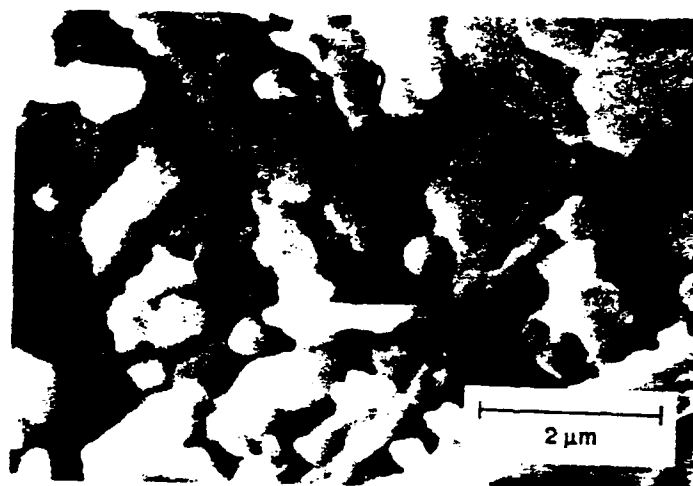


FIGURE 1

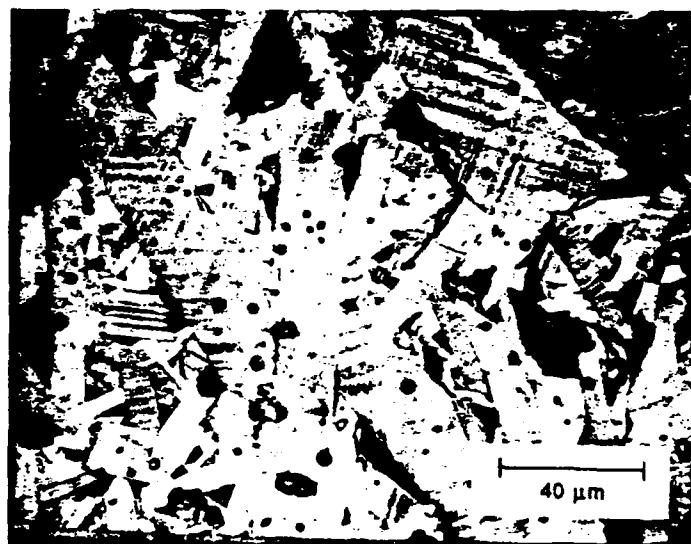
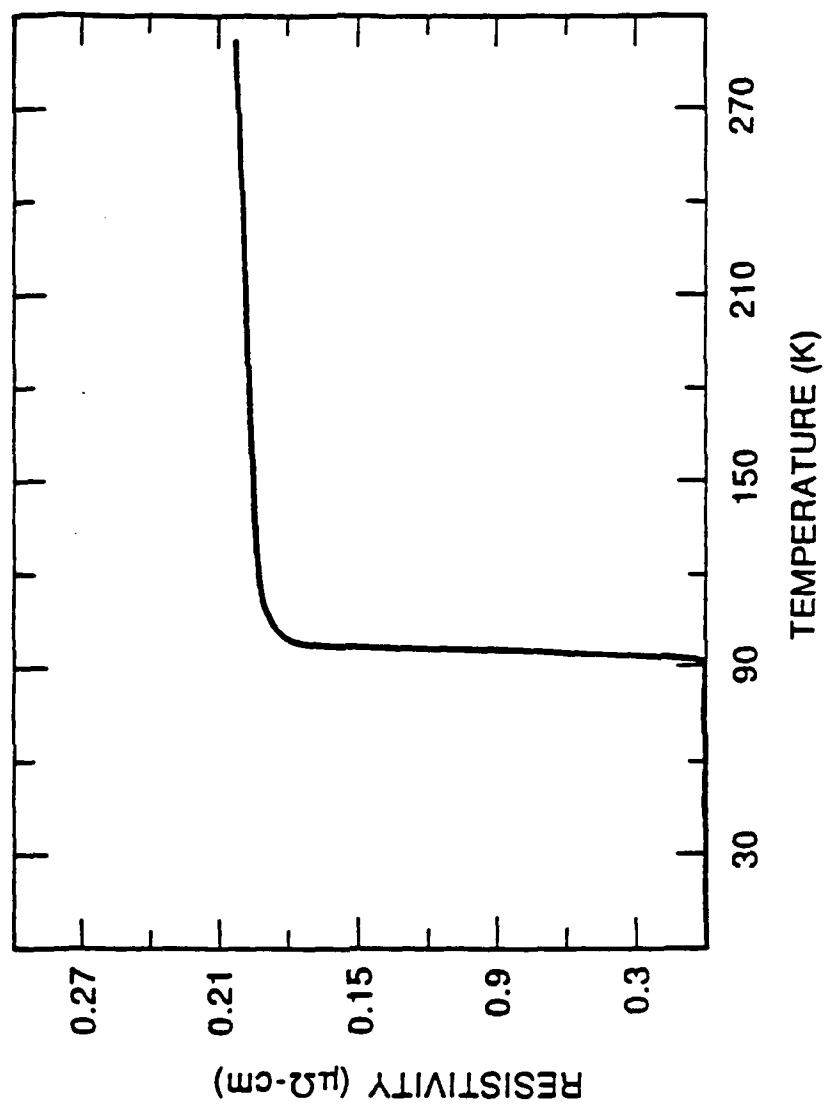
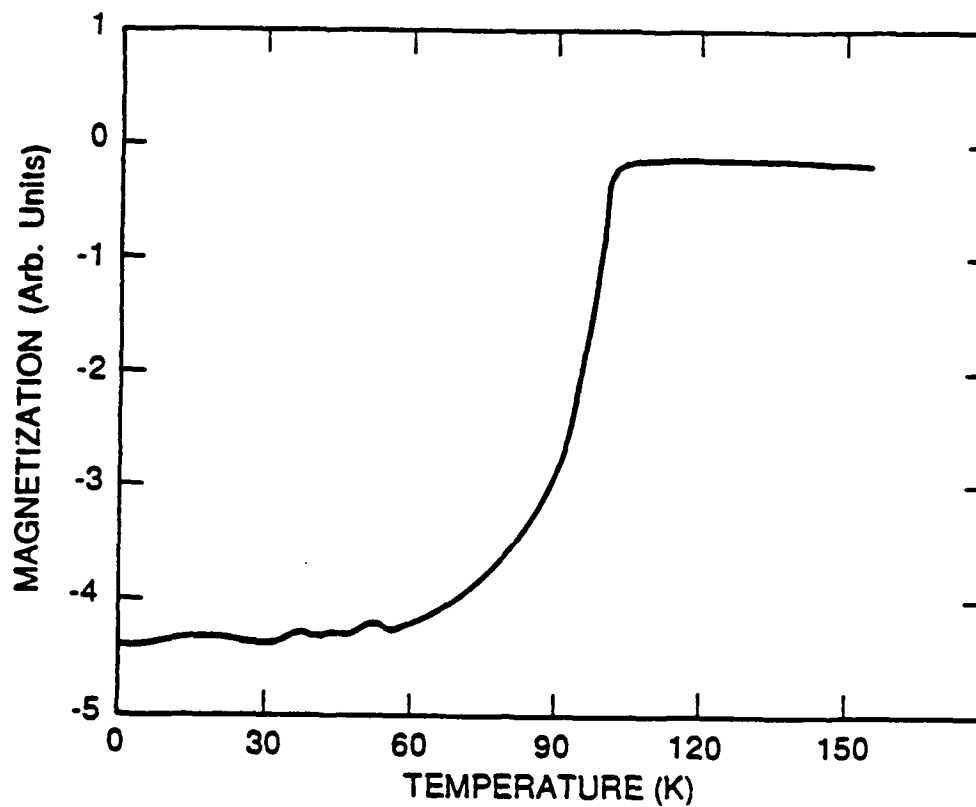


FIGURE 2

FIGURE 3



**FIGURE 4**

CRYOCHEMICAL METHOD OF PREPARING ULTRAFINE PARTICLES OF HIGH-PURITY SUPERCONDUCTING OXIDES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to superconducting ceramic particles. More particularly, it pertains to a method of preparing small particles of high-purity superconducting oxides, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ ($d=0$ to 1), by a freeze-drying technique, which involves atomizing an aqueous solution of the soluble salts onto liquid nitrogen, followed by subliming of the frozen water, calcining and heating in air or oxygen.

2. Description of Related Art

Most reports on the preparation of superconducting ceramic oxides indicate that only crude methods of powder preparation are used, such as calcining the oxide followed by mechanical grinding. The powders produced by these methods are not ideal according to conventional practice. Major problems associated with these powders include inhomogeneity, non-uniformity in terms of particle size, shape, high impurity levels e.g., from milling, and lack of reproducibility. Conducting materials fabricated from these powders may exhibit some superconducting behavior; however, the current densities are usually low and the microstructure is far from controllable. Anomalies in superconducting behavior are often traced to the powder and its size.

An overview of the recent progress in the preparation of superconducting ceramic oxides by Ron Dagani is found in *Chemical and Engineering News*, pp 7-16, published May 11, 1987, which is incorporated herein by reference. The new materials are metal oxide ceramics, usually having a perovskite-like or spinel-like structure, which can conduct electricity with virtually no resistance at temperatures at or above the boiling point of liquid nitrogen (77K or -196°C). These materials are useful to conduct electricity for hundreds of miles with no dissipative losses, and no heating up of the transmission lines. These superconductors would also be useful in supercomputers, in magnetically levitated high speed trains, improved nuclear magnetic resonance scanners, and the like.

F. R. Monforte et al., in U.S. Pat. No. 3,516,935 disclose a method of freeze-drying an aqueous solution of soluble salts. It discloses methods of forming the solution, droplet formation, freezing, collection of the frozen droplets, sublimation, conversion, forming and firing. By following the methods described, one would not obtain superconducting powders.

F. R. Monforte et al., in U.S. Pat. No. 3,551,533 disclose a preparation of particulate matter by freeze-drying an atomized solution of soluble salts. A number of solute, solution, freezing, collection, sublimation, conversion, and crushing conditions are described. Sizes of particles range from 1 micron to 0.4 millimeters. This patent does not disclose the process by which superconducting oxide powders are obtained.

A. Lansberg in U.S. Pat. No. 3,357,819 discloses a process of preparing homogenous powders composed of ultrafine particles. A solution or dispersion of the salts are freeze dried by dripping into a cold solution, e.g. liquid nitrogen, followed by sublimation of the water from the particles. The patent does not refer to

any subsequent treatment of the particles which is necessary to obtain superconducting oxides.

A. W. Sleight in U.S. Pat. No. 3,932,315 discloses superconductive barium-lead-bismuth oxides of the formula $\text{Ba}_{1-x}\text{A}_x\text{Pb}_{1-y}\text{Bi}_y\text{O}_3$ wherein A is sodium, potassium, rubidium, cesium, strontium or lead, x is 0 to about 0.5 and y is about 0.05-0.3. The temperature marking the onset of superconductivity is low, a maximum of 13K.

J. Kelly et al., in the *Journal of Materials Science*, Vol. 13, pp. 1053-1060, published in 1978, disclose a study of a cryochemical method for the preparation of high surface area perovskite semiconducting powders. An aqueous solution is rapidly frozen in liquid nitrogen, followed by a vacuum sublimation of the ice. The sequence of steps necessary to obtain particles of a superconducting oxide of the present invention is not disclosed.

D. W. Johnson et al., in the *Ceramic Bulletin*, Vol. 53, No. 2, pp. 163-167, published in 1974, disclose the effect of preparative techniques and calcination temperatures on some lithium ferrites. The properties of the particles which were (1) sprayed dried, (2) freeze-dried or (3) co-precipitated were compared. This reference does not disclose the preparation of superconducting powders.

A. C. C. Tseung et al., in the *Journal of Materials Science*, Vol 5, pp. 604-610, published in 1970, disclose the preparation of high surface area lithium doped nickel oxide particles by spraying an aqueous solution of the salts into liquid nitrogen followed by sublimation and heating at 300°C - 1000°C to produce the lithium nickel oxide. When silver chloride is present, a large excess of ammonia, to pH 2 or lower, is used to solubilize the silver ion. The materials nor the conditions described disclose or suggest a method of obtaining particles of a super conducting oxide.

V. V. Mirkovich et al., in *Ceramic Bulletin*, Vol. 49, (#8), pp 724-725, published in 1970, disclose the cryochemical method of preparing ceramic raw materials such as $\text{Al}_2(\text{SO}_4)_3 \cdot \text{MgSO}_4$ by spraying into stirred liquid nitrogen. The particles obtained have a spherical form which varies in size between 50 and 500 micrometers.

P. D. S. St. Pierre et al. in U.S. Pat. No. 3,026,177 disclose a method for producing particles of transparent polycrystalline high density alumina. This patent does not disclose a preparation of superconducting oxides.

Y. S. Kim et al., in the *Ceramic Bulletin*, Vol. 50 (#6), pp. 532-535, published in 1971 disclose a cryochemical preparation of powders of polycrystalline alumina.

H. A. Sauer et al., in the *American Institute of Chemical Engineering Journal*, Vol. 18 (#2), pp 435-437, published in 1972, disclose a cryochemical process to prepare particles of aqueous solutions. The droplets are introduced into the lower region of the cooled stirred liquid and rise up through an immiscible nonflammable refrigerant.

S. R. Ovshinsky et al., in *Physical Review Letters*, Vol 58 (#24), pp 2579-2081 disclose a superconducting oxide of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{F}_x\text{O}_7$ having a T_c at 155K. However, other researchers have thus far been unable to repeat this result.

T. H. Geballe et al., in "Some Thoughts About the High T_c Perovskite Superconductors", in the Extended Abstracts for the MRS Symposium in High Temperature Superconductors, Anaheim, Cal., Apr. 23-24, 1987, disclose some physical properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$, where d is 0-1. The bulk sample was reported only as being prepared by a freeze-drying method. No addi-

tional description of the experimental details of the method was disclosed.

Other general methods of forming ceramic particles, alloys and bodies are described in U.S. Pat. No. 3,026,210; 3,748,728; 4,073,666; 4,264,358; 4,508,752; 5 and 4,581,289.

It is usually observed that as the size of the particles of the superconducting compounds get larger, that superconducting properties become smaller. Powders having a size of 100 microns or larger (e.g. 200 microns) 10 have reduced or vanishing small superconducting properties. These are the general sizes of the superconducting powders produced by methods of the art described above. Powder having a size of about 10 microns or less 15 show useful superconducting properties. This is the size of the powders obtained in the present invention.

All of the above 20 references are incorporated herein by reference for general information in this art.

None of the references cited hereinabove separately or in combination disclose, teach or suggest the method 20 of producing a superconducting oxide as is described by the present invention.

It is therefore an object of the invention to provide a method of producing a superconducting oxide by mixing 25 soluble aqueous salts to form a solution, atomize this aqueous solution onto liquid nitrogen, remove the liquid nitrogen, remove the ice present by sublimation under reduced pressure, calcine the solid crystals and then heat at 800°-890° C. and cool to ambient temperature to obtain a superconducting oxide having a T_c of 77K or 30 higher and a size of between about 0.05 and 10 microns. The present invention provides such an improved process.

SUMMARY OF THE INVENTION

The present invention relates to a method of preparing particles of superconducting ceramic powders, which method comprises:

- (a) dissolving the soluble salts of cations in aqueous medium;
- (b) obtaining a solution having a pH of between about 4 and 7 by optionally treating the aqueous medium with ammonia or ammonium hydroxide;
- (c) atomizing the solution of step (b) onto liquid nitrogen at about -196° C. producing particles of the 45 mixed salts and ice;
- (d) removing the liquid nitrogen by evaporation;
- (e) removing the water from the solid of step (d) by sublimation at reduced pressure under conditions which preclude melting or coalescence of the particles;
- (f) heating the solid residue of step (e) at about 40°-60° C. at reduced pressure;
- (g) calcining the solid residue in sufficient oxygen or air at temperature of between about 200° and 895° C.; 55 and
- (h) cooling slowly the solid from a temperature of about 895° C. to about ambient temperature in sufficient air or oxygen and recovering the superconducting powder having an average diameter of between about 0.1 60 and 10 microns.

In another embodiment, optionally, substep (h), additionally includes during cooling, the annealing of the particles in sufficient oxygen or air at between about 200° and 500° C. for between about 2 and 30 hrs. 65

In another embodiment, the present invention relates to superconducting particles having a structure comprising:



wherein:

A and A' are each independently selected from lanthanum, yttrium, samarium, europium, gadolinium, dysprosium, holmium or mixtures thereof;

B and B' are each independently selected from barium, strontium-calcium, barium-strontium or barium-calcium;

D is selected from platinum, copper, silver, tin or mixtures thereof;

X and X' are each independently selected from oxygen, fluorine or mixtures thereof;

j is between about 0.7 and 4;

k is between about 1.6 and 4;

m is between about 2.6 and 6; and

n is between 4 and 15.

Preferably the final particles have spinel-like or a perovskite-like structure. Perovskite-like is preferred. These superconducting ceramic powders have a T_c above 77K and generally have a size in the range of 0.1 to about 10 microns, preferably about 0.5 to 2 microns.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 shows the appearance of the powder at ambient temperature, $YBa_2Cu_3O_{7-d}$ ($d=0-1$), immediately after calcination at 825° C. before milling having a grain size of about or less than 2 microns (about 0.1 to 2 microns).

FIG. 2 shows the appearance of the powder at ambient temperature, $YBa_2Cu_3O_{7-d}$ ($d=0-1$), after it is sintered at 925° C., which material is heavily twinned with particles as large as 100 micrometers.

FIG. 3 is an example of the resistivity-temperature curve for a sintered sample of the ceramic oxide, $YBa_2Cu_3O_{7-d}$ ($d=0-1$).

FIG. 4 is an example of the Meissner effect curve for the sintered sample of ceramic oxide, $YBa_2Cu_3O_{7-d}$ ($d=0-1$).

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENT

Definitions

As use herein:

"Annealing" refers to heating at between about 200° and 700° C. an inorganic oxide in sufficient air or oxygen to add oxygen to the lattice structure, and stabilize the oxide at the same time the superconducting properties are stabilized.

"Atomizing" refers to the procedure of producing very fine particles usually of a liquid. It can include spraying through a nozzle, through a rotating disc, by ultrasonication or the like.

"Calcining" refers to heating a salt sample having an inorganic component at a temperature usually greater than 500° C. to remove gases. That is, a portion of the metal compound is oxidized, and is evolved as a gas, leaving a metal oxide residue, e.g. $Ca(NO_3)_2 \rightarrow 2CuO + 2NO_2$. Calcining is performed by observing the change in the weight of sample, and is complete when the weight of the heated sample remains constant.

"Cations" refers to those metal, transition metal, rare earth, alkaline earth cations which are useful to produce superconducting materials, such as oxides and/or fluorides. Cations includes but is not limited to lanthanum, yttrium, samarium, europium, gadolinium, dysprosium,

holmium and the like. Mixtures of these cations are included. Additional cations include barium and mixtures of strontium, calcium and barium. Other cations include platinum, copper, silver, tin, and the like. Mixtures are contemplated. The cations and their mixtures usually in aqueous solution, are soluble in the presence of each other or produce a finely divided suspension which is suitable for atomizing. To obtain specific ratios of the cations in the final powders, one usually combines cations of like ratios in the aqueous solutions prior to atomizing.

"Ceramics" refers in, the ceramic of the present invention to mixed cation oxides, mixed cation halides, especially fluorides, or mixtures of oxides and fluorides. Ovshinsky et al., above, which is incorporated herein by reference, describes superconductors wherein about one in four oxygen atoms in $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ is replaced by a fluorine atom. Other reported superconducting compounds include $\text{YBa}_2\text{Cu}_3\text{O}_6\text{F}$. The method of preparing superconducting compounds of the present invention include these superconductors having mixtures of oxygen and other atoms, such as oxygen-fluorine, which are superconducting above 77K.

"Optionally" or "optional" refers to an event or to a step which may or may not take place within the invention, or to a chemical or a component which may or may not be present.

"Perovskite" or "perovskite-like" refers to the class of minerals or compounds that relate in structure to CaTiO_3 or MgSiO_3 . The superconducting ceramic, however, is usually a distorted, oxygen deficient form of perovskite with a layered structure not generally seen in naturally occurring minerals. On a simplistic level, the structure consists of near-planar arrays of metal (copper) and oxygen atoms. The metal atoms usually exist in different valence states. Because of this variability, the number of oxygen atoms also varies so that the oxygen's total negative charge balances the metal's positive charge.

PREPARATION OF THE SUPERCONDUCTING OXIDE PARTICLES-OXIDE

Although oxide is used in the following description, it is to be understood that oxides, fluorides, chlorides, bromides, sulfates, etc. can be used. The superconducting powder oxide can be an oxide, a fluoride, a mixture of oxide-fluoride and the like.

Step (a):

The soluble salts of the cations are weighed accurately and mixed with distilled or deionized water. Concentrations of each cation in solution is between about .015 and 0.15 molality. Both organic and inorganic salts are considered within the invention. Useful organic salts include for example, acetates, citrates, propionates, oxalates, tartrates, fumarates and the like. The acetates are generally preferred. The useful inorganic salts include the oxides, hydroxides, chlorides, fluorides, bromides, nitrates, carbonates, sulfates and the like. Generally, the nitrates are preferred. The sulfates are often only sparingly soluble, particularly BaSO_4 . Thus, barium acetate is usually the salt of choice.

These salts need to be of high purity and free of interfering ions. The purity of the salts ranges from about 99.0 to 99.999% or higher and are available from chemical supply houses and are used as provided without additional purification.

A fine aqueous suspension or colloid of the salts is also contemplated in the present invention. These salts

when used in the method of the present invention will produce fine particles of superconducting oxides.

In one embodiment, the superconducting oxides produced have the formula:



wherein:

A and A' are each independently selected from lanthanum, yttrium, samarium, europium, gadolinium, dysprosium, holmium or mixtures thereof;

B and B' are each independently selected from barium or strontium-calcium, barium-strontium, or barium-calcium;

D is selected from platinum, copper, silver, tin or mixtures thereof;

x is about 1;

y is about 2;

z is about 3, and

q is about 7-d, where d is 0-1.

Thus, A or A' is nitrate or organic salts of lanthanum, yttrium, samarium, europium, gadolinium, dysprosium, holmium, or mixtures thereof. Primarily, the salts need to evolve a gas to produce the oxide when calcined at about 500°-700° C. Yttrium and lanthanum nitrates are preferred.

The starting salts for the B or B' component is barium nitrate or barium organic salt. Other starting salts include mixtures of strontium acetate-calcium acetate, barium acetate-strontium acetate, or barium acetate-calcium acetate.

The starting salts for the D component of the superconducting oxide include platinum, copper, tin or silver nitrates. It is also possible to have mixtures of these salts such as copper-tin. Copper nitrate is preferred.

Some of the solutions are heated to about 90° C., e.g. BaNO_3 , and all solutions are stirred for between about 2 and 16 hours (for convenience - overnight) at about 90° C.

Generally, commercial considerations require the use of concentrations of the salts near the saturation limit in the liquid phase at the freezing temperature of the solution. If the concentration of the cations in solution is reduced, the time necessary to remove the water/ice from the crystals becomes longer. Also increased expenditures for larger equipment, electricity, and the like are necessary to remove the large volume of solvent.

Step (b):

It was determined that obtaining a pH of the mixed solutions of cations of between about 4 and 7 was beneficial to the method. The sparingly soluble salts usually remained in solution. The control of pH also aids in the subsequent steps in that it aids in preventing the melting and/or coalescence of the particles. If melting or coalescence occurs in steps (c) to (h), usually the particles become too large to be readily sintered or to be useful super-conductors. If the mixture of salts do not produce a solution having a pH of between about 4 and 7, preferably between about 4 and 5, then ammonia or concentrated ammonium hydroxide is added to obtain the desired pH.

Step (c):

Next the aqueous solution is atomized, usually by spraying, onto liquid nitrogen at about -196° C. at ambient pressure. Usually contact with atmospheric moisture is not a problem. However, a nitrogen or helium atmosphere may be used if desired. The spray nozzle used is a standard thin layer chromatography

spray nozzle (one source is from Wheaton Scientific of 1000 Tenth Street, Millville, N.J. 08332. The spray atomizer should be able to produce a fine spray of particles onto the liquid nitrogen. The liquid sprayed droplets generally have a size of between about 1 and 10 microns, although large and smaller droplets are useful. The pressure for the spray is provided by nitrogen; usually about 10-20 psig.

Generally, the solutions of the cations A, B and D are mixed and sprayed as a single solution. The cations of A, B and D are compatible and may or may not precipitate on standing at ambient temperature.

In one embodiment (b'), it is possible to have two or more cations in one solution and one cation in a separate solution. These three cation solutions are marginally compatible when mixed and allowed to stand. In this alternative technique, the two or more solutions are joined in a single mixing chamber in the spray line and are in contact with each other for about 60 seconds or less before being freeze-dried by spraying onto the liquid nitrogen. Some improvements in the final superconducting particles is seen in the powders prepared by this technique.

Thus, in one example, barium acetate and yttrium nitrate are combined to produce aqueous one solution. Copper nitrate aqueous solution is kept separate. The two solutions are atomized onto liquid nitrogen after mixing in the line about 30-60 seconds.

Step (d):

The liquid nitrogen is then removed by evaporation, usually at ambient pressure. However, if desired a vacuum of between about 700 and 1 mm of mercury may be employed. Gentle heat may also be added to speed the evaporation, e.g. placing the particles (liquid nitrogen) in a -50° C. chamber.

It is critical that the ice-inorganic crystals formed do not melt or coalesce during this liquid nitrogen evaporation.

Steps (e) and (f):

The frozen beads (particles or crystals) are then subjected to a vacuum of less than about 200 mTorr and then slowly heated to about 40°-60° C. at about 5° C./min while the ice is removed by sublimation under vacuum. It is very important that the crystals do not melt or coalesce into larger particles at this stage. Control of the pH as described above usually prevents this melting problem. The particles tend to be hygroscopic after freeze-drying, and it is necessary to calcine the particles immediately to maintain small particle size.

Step (g):

After the ice is removed and the particles are gently heated, the particles are then calcined in oxygen (up to 100%), which is optionally flowing) (or about 1.5 l/min) or air (which is optionally flowing) at a temperature of about 200 to 825° C. to obtain a constant weight. The particles are then heated up to 825°-895° C. in oxygen or air (which are optionally flowing) to obtain a perovskite-like structure.

Step (h):

The particles are next cooled slowly from about 895° C. to ambient temperature in sufficient oxygen or dry air. The particles (powders) generally have a diameter of between about 0.1 and 10 microns. When cooled to -196° C. or a higher (+) temperature, these particles exhibit superconductivity at temperatures greater than 77K.

In some instances, the particles in step (h), during the cooling, are held at between about 200° and 500° C. and

annealed in flowing oxygen or air for between about 2 and 30 hrs.

It is determined in later experiments that the environment for heating above 200° C. in steps (g), (h), (G) and (H) herein needs only to contain oxygen. This is achieved by an oxygen or air environment in amounts sufficient to provide the oxygen to form the perovskite or perovskite-like structures. Flowing oxygen or air are methods to make certain that sufficient oxygen is present to form the desired oxygen-containing structures which have super conducting properties.

Weight loss studies indicate that calcination is essentially complete in 1 hr at 700° C. For longer times, there is evidence of some small weight gain. However, x-ray diffraction (XRD) indicates that only a small amount of the desired phase forms at this low temperature (700° C.) even after 49 hrs. Calcination and reaction at 825° C. for a time in excess of about 12 hrs results in the formation of the desired phase (perovskite) as evidenced by a very sharp X-ray pattern. FIG. 1 shows the appearance of particles of the present invention immediately after calcination, but without any milling. Individual particles range from less than about 0.5 microns to 1 micron. Some agglomeration is evident but light milling (e.g. low speed planetary ball milling for 15 minutes) readily breaks up these agglomerates.

Substantial sintering does not occur at 700° C., and samples sintered at these temperatures exhibit relatively poor Meissner effects. Sintering at 890° C. for 24 hrs. produced densities ranging from about 80 to 86% of the theoretical value. Higher densities, up to about 89% (of theoretical density of 6.36 g/cm³) were achieved by sintering at 925° C. for about 12 hrs.

The difference in the microstructure of the powders caused by the increase of about 25° to 35° C. (900°-925° C.) in the sintering temperature is very great. Samples sintered at about 890° C. had very fine microstructure with grain sizes of less than about 2 microns. Samples sintered at 925° C. had some grains as large as 100 microns with high aspect ratios. Evidently, at about 900° C. or above the particles tend to melt and/or coalesce. These grains, as shown in FIG. 2, are heavily twinned and have grown very rapidly as shown by the number of included pores. A small amount of second phase is present along grain boundaries and in triangular pockets. Analysis of this phase by energy dispersion X-ray analysis (EDAX) indicated that it is Cu rich and Y poor in comparison to the major phase. A preliminary phase diagram for the baria-yttria-copper oxide system indicates that there is a region of partial melting associated with compositions toward the Cu-rich, Y-poor side of the "1-2-3" phase, and that melting occurs in the range of 875°-950° C. The coarse grains and the appearance of the second phase that appears to wet some boundaries is consistent with partial melting and associated change in sintering behavior.

An example of the resistivity-temperature curve for a sintered sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ (where $d=0$ to 1) (890° C. for 24 hr) is shown in FIG. 3. The resistivity drop-off in the ceramic samples made from the cry-chemically produced powders is sharp, ranging from between 1-3K and the transition temperatures are in the range of 90-96K.

An example of the Meissner effect curve for a sintered sample (890° C., 24 hr) of $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ is shown in FIG. 4. The ceramic powder has a relatively sharp Meissner effect, greater than 60% of the shielding signal.

Qualitative measurements of the Meissner effect, as evidenced by levitation distances, are performed on a number of ceramic samples. The measurements, which are generally comparative, indicate that a heat treatment of about 12 to 24 hrs. at about 400° C. or higher (preferably in flowing oxygen or air) will restore superconducting behavior of a sample of oxide which has deteriorated as a result of exposure to the atmosphere. In addition, this oxygen/heat treatment will cause previously non-superconducting samples (improperly handled or heated samples) to become superconducting. Further, the oxygen/heat treatment would increase the levitation effect on superconducting powders. Weight gains during oxygen/heat treatment of about 2-8 percent were found in a series of sintered samples treated with flowing oxygen (1.5 l/min) for 39 hrs. at 400° C. The largest weight gains were associated with the greater apparent increase in superconducting properties.

The ceramics produced by this method have small particle size, high purity, homogeneity and reactivity. The method is suitable for producing commercial quantities of superconducting ceramic, with batch size runs of 50-100 g easily achieved in the laboratory.

It is to be understood that the ceramic powders produced in this invention can have approximate compositions such as, $Y_{1.2}Ba_{0.8}CuO_4$, $YBa_2Cu_3O_w$, where w is between 6.5 and 7.2, etc. Preferred compositions are also described herein.

The following Examples are meant to be illustrative and representative only, and are not to be construed to be limiting in any way.

EXAMPLE 1

Preparation of $YBa_2Cu_3O_{7-d}$ (d=0-1)

(a) To a 2,500-ml beaker at STP containing a magnetic stirring bar and 1000 ml of distilled water is added 66.833 g of barium acetate (0.262 mol, 99.9% purity from Johnson-Matthey of Seabrook, N.H.). Yttrium nitrate, (99.9%) 50.00 g (0.131 mole) also from Johnson-Matthey, in 500 ml of distilled water is added next. Next is added 100 g of copper nitrate $\cdot 3H_2O$ (0.393 mol of 99% purity), also from Johnson-Matthey. The components are all in solution after heating at 90° C. for 16 hrs. (overnight), pH about 4. The two liters of solution are spray atomized onto 4 liters of liquid nitrogen using a thin layer chromatography spray nozzle, over a 2.5 hr. period. The liquid ammonia is then removed by evaporation using a slight vacuum. While the ice/salt crystals are still at a very low temperature. A vacuum system is attached, and the ice is sublimed at 150 mTorr. Next, the solid is allowed to heat for 4-16 hrs. at 40°-60° C. under a vacuum of 300 mTorr. The sample is immediately calcined in flowing oxygen starting at 200° C. and increasing the temperature to 895° C. over a 4 hr. period. The oxides formed are then cooled in flowing oxygen (1.5 l/min.) to ambient temperature. The particles obtained have a size of between about 0.5 and 2 microns. When the oxide, $YBa_2Cu_3O_{7-d}$ where d is 0-1, is tested for superconductivity, the oxide has a T_c of about 94K (see FIG. 3).

(b) The procedure of Example 1(a) is repeated except, the molarity of the salts is doubled, and that after the salts are combined 14.3 ml of aqueous concentrated ammonia is added to produce a pH of 4.5. The powder obtained is essentially equivalent to that obtained in Example 1(a).

EXAMPLE 2

Preparation of Superconducting Oxides

(a) Similarly as described above in Example 1(a) the procedure is repeated except that the yttrium nitrate is replaced by a stoichiometrically equivalent amount of:

- (i) lanthanum;
- (ii) samarium;
- (iii) europium;
- (iv) gadolinium;
- (v) dysprosium; or
- (vi) holmium.

It is expected that superconducting solid particles comparable to $YBa_2Cu_3O_{7-d}$ (d is 0 to 1) will be obtained.

(b) Similarly as is described in Example 1(b) the procedure repeated, except that the yttrium nitrate is replaced by a stoichiometrically equivalent amount of:

- (i) lanthanum;
- (ii) samarium;
- (iii) europium;
- (iv) gadolinium;
- (v) dysprosium; or
- (vi) holmium.

It is expected that superconducting solid particles comparable to $YBa_2Cu_3O_{7-d}$ (d is 0 to 1) will be obtained.

EXAMPLE 3

Preparation of Superconducting Oxides

(a) Similarly as is described above in Example 1(a) the procedure is repeated except that the barium acetate is replaced by stoichiometrically equivalent amount of a 50/50 mixture of:

- (i) strontium acetate - calcium acetate;
- (ii) barium acetate - strontium acetate; or
- (iii) barium acetate - calcium acetate. It is expected that superconducting solid particles comparable to $YBa_2Cu_3O_{7-d}$ (d is 0-1) will be obtained.

(b) Similarly as is described in Example 1(b) the procedure is repeated except that the barium acetate is replaced by stoichiometrically equivalent amount of a 50/50 mixture of:

- (i) strontium acetate - calcium acetate;
- (ii) barium acetate - strontium acetate; or
- (iii) barium acetate - calcium acetate. It is expected that superconducting solid particles comparable to $YBa_2Cu_3O_{7-d}$ (d is 0-1) will be obtained.

EXAMPLE 4

Preparation of Superconducting Oxide

(a) Similarly as is described in Example 1(a) above, the procedure is repeated except that the copper nitrate is replaced with a stoichiometrically equivalent amount of:

- (i) platinum,
- (ii) silver; or
- (iii) tin.

It is expected that the superconducting oxide obtained will be comparable to $YBa_2Cu_3O_{7-d}$ where d is 0-1.

(b) Similarly as is described in Example 1(b) above, the procedure is repeated except that the copper nitrate is replaced with a stoichiometrically equivalent amount of:

- (i) platinum,
- (ii) silver; or
- (iii) tin.

It is expected that the superconducting oxide obtained will be comparable to $\text{YBa}_2\text{Cu}_3\text{O}_{(7-d)}$ where d is 0-1.

EXAMPLE 5

Freeze-Dry Atomizing Using Two Solutions after Immediate Mixing

(a) To separate 500 ml aqueous solutions are added yttrium salt (0.1 Molar in Y), barium salt (0.2 M in Ba) are combined and placed in a glass burette. A Cu salt solution (0.3 M in copper 500-ml) is placed in a separate burette. The burettes are connected using TYGON tubing and a glass Y-joint. The solutions are combined and mechanically mixed for less than 60 seconds at the Y joint then atomized using a thin layer chromatographic spray head. The flow-rates for spraying and subsequent steps were performed as described in Example 1(a) above. The superconducting powder obtained after heat treating at 825° C. has the same structure as found in Example 1(a) above.

While the present invention has been described with reference to the specific embodiments thereof, it should be understood by those skilled in the art of preparing uniform ultrafine powders and particles as described herein, and their use as superconductors that various changes may be made and equivalents may be substituted without departing from the true spirit and scope of the present invention. In addition, many modifications may be made to adapt a particular situation, material, or composition of matter, process, process step or steps to the spirit and scope of this invention, without departing from its essential teachings.

We claim:

1. An improved method of preparing fine particles of superconducting ceramic powders, which method comprises:

- (a) dissolving the soluble salts of cations in aqueous medium;
- (b) obtaining a substantially saturated solution of the salts and adjusting the pH to between about 4 and 7;
- (c) atomizing the solution of step (b) onto liquid nitrogen at about -196° C.;
- (d) removing the liquid nitrogen by evaporation of the nitrogen under reaction conditions such that the ice-salt crystals do not coalesce into larger particles;
- (e) removing the ice by sublimation at reduced pressure under reaction conditions such that the ice-salt crystals do not melt;
- (f) heating the solid residue of step (e) at about 40°-60° C. at reduced pressure under the reaction conditions such that the residue does not melt;
- (g) calcining the solid residue in sufficient oxygen or air at temperature of between about 200° and 895° C.; and
- (h) cooling slowly the solid at a temperature of between about 900° C. and ambient temperature in sufficient air or oxygen concurrently annealing the particles in flowing oxygen or air at between about 200° and 500° C. for between about 2 and 30 hrs and recovering the superconducting solid powder having an average diameter of between about 0.1 and 10 microns.

2. The method of claim 1 wherein in substep (b) the pH of about 4 to 7 of the aqueous solution is obtained by treating the aqueous medium with ammonia or ammonium hydroxide.

3. The method of claim 1 wherein the particles have a spinel or perovskite-like structure comprising:



wherein:

A and A' are each independently selected from lanthanum, yttrium, samarium, europium, gadolinium, dysprosium, holmium or mixtures thereof;

B and B' are each independently selected from barium, strontium-calcium, barium-strontium or barium-calcium;

D is selected from platinum, copper, silver, tin or mixtures thereof;

x is about 1;

y is about 2;

z is about 3; and

q is 7-d, where d is between 0 and 1.

4. The process of claim 1 wherein in step (b) the pH is between about 4 and 5.

5. The process of claim 1 wherein in step (a) the soluble salts are selected from organic and inorganic salts.

6. The method of claim 5 wherein in step (a) the soluble salts are selected from nitrates or acetates.

7. The process of claim 5 wherein the concentration of the soluble salts is between about 0.015 and 0.15 molar.

8. The process of claim 7 wherein A and A' are each yttrium.

9. The process of claim 8 wherein D is copper.

10. The process of claim 9 wherein B and B' are each barium.

11. A method for producing particles of superconducting ceramic powders having a superconductivity transition temperature (T_c) of about 77K or greater, which method comprises:

(A) dissolving the compatible soluble salts of the cations selected from nitrates or acetates in an aqueous medium;

(B) obtaining a solution having a pH between about 4 and 7;

(C) spray atomizing the solution of step (B) onto liquid nitrogen at about -196° C.;

(D) removing the liquid nitrogen as a gas at about ambient temperature by evaporation without melting or coalescence of the ice-salt crystals;

(E) removing the ice from the ice salt crystals by sublimation at reduced pressure without melting or coalescence of the ice-salt crystals into larger particles;

(F) drying the salt crystals obtained in step (E) to about 40°-60° C. in a vacuum without melting or coalescence of the salt crystals;

(G) calcining the solid residue of step (F) in sufficient oxygen or dry air at a temperature between about 200° and 895° C.; and

(H) cooling slowly the solid of step (G) in an anhydrous atmosphere in sufficient oxygen or air to ambient temperature concurrently annealing the particles in sufficient oxygen or air at between about 200° and 700° C. for between about 2 and 30 hrs, and recovering the superconducting solid powder having an average diameter of between about 0.1 and 10 microns.

12. The method of claim 11 wherein in step B the pH is obtained by contacting the aqueous medium with sufficient ammonia or ammonium hydroxide.

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13. The process of claim 11 wherein the ceramic powder consists essentially of a ceramic oxide of the formula:



wherein:

A is selected from lanthanum, yttrium, samarium, europium, gadolinium, dysprosium, holmium, or mixtures thereof;

B is selected from barium, strontium-calcium, barium-strontium, or barium-calcium;

D is selected from copper, platinum, silver, tin, or mixtures thereof;

x is about 1;

y is about 2;

z is about 3; and

q is about 7-d, where d is 0-1.

14. The process of claim 11 wherein in step (A) the concentration of each soluble salt is between about 0.02 and 0.15 molal.

15. The process of claim 13 wherein A is yttrium.

16. The process of claim 15 wherein B is barium.

17. The process of claim 16 wherein C is copper.

18. The process of claim 11 wherein the ceramic particles of step (H) have an average diameter of between about 0.5 and 5 microns.

19. The process of claim 18 wherein the ceramic particles of step (H) have a diameter of between about 0.1 and 1.5 micron.

20. A method of preparing particles of superconducting ceramic powders, which method comprises:

(a) dissolving the soluble salts of the cations in two or more separate aqueous media;

(b) obtaining separate cation solutions having pH of about 4 and 7;

(b') mixing the separate solutions of steps (a) and (b) intimately for about 60 seconds then immediately;

(c) atomizing the solution of step (b') onto liquid nitrogen at about $-196^{\circ}\text{C}.$;

(d) removing the liquid nitrogen by evaporation under conditions such that the ice-salt crystals do not coalesce into larger crystals;

(e) removing the ice by sublimation at reduced pressure under reaction conditions such that the ice-salt crystals do not coalesce into larger particles;

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(f) heating the solid residue of crystals of step (e) to about $40^{\circ}\text{--}60^{\circ}\text{C}.$ at reduced pressure;

(g) calcining the solid residue in sufficient oxygen or air at temperature of between about 200° and $895^{\circ}\text{C}.$; and

(h) cooling the solid at a temperature of between about $900^{\circ}\text{C}.$ and ambient temperature in sufficient air or oxygen concurrently annealing of the particles in sufficient oxygen at between about 200° and $500^{\circ}\text{C}.$ for between about 2 and 30 hrs and recovering the superconducting solid powder having an average diameter of between about 0.1 and 10 microns.

21. The method of claim 20 wherein in substep (b) the pH is obtained by treating the aqueous medium with ammonia or ammonium hydroxide.

22. The method of claim 1 wherein the particles have a structure comprising:



wherein:

A and A' are each cations independently selected from lanthanum, yttrium, samarium, europium, gadolinium, dysprosium, holmium or mixtures thereof;

B and B' are each cations independently selected from barium, strontium-calcium, barium-strontium or barium-calcium;

D is a cation selected from platinum, copper, silver, tin or mixtures thereof;

X and X' are each independently selected from oxygen, fluorine or mixtures thereof;

j is between about 0.7 and 4;

k is between about 1.6 and 4;

m is between about 2.6 and 6; and

n is between 4 and 15.

23. The method of claim 22 wherein the particles after step (h) have a spinel or perovskite-like structure.

24. The method of claim 1 wherein in step (a) the cations are selected from metal cations, transition metal cations, rare earth cations or alkaline earth cations or mixtures thereof which are useful to produce superconducting materials.

25. The method of claim 24 wherein the cations are selected from metal cations.

26. The method of claim 1 wherein at least five cation solutions are mixed in substep (a).

* * * * *

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United States Patent [19]

Gusman et al.

US005122505A

[11] Patent Number: 5,122,505

[45] Date of Patent: Jun. 16, 1992

[54] CARBONATE-FREE INORGANIC NITRATES OR OXIDES AND PROCESS THEREOF

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[21] Appl. No.: 591,036

[22] Filed: Oct. 1, 1990

[51] Int. Cl.⁵ H01L 39/12

[52] U.S. Cl. 505/1; 505/725; 505/734; 505/737; 505/780; 252/521; 423/593; 501/123

[58] Field of Search 505/1, 725, 734, 737, 505/780; 252/521; 423/593; 501/123

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Primary Examiner—Paul Lieberman

Assistant Examiner—Bradley A. Swope

Attorney, Agent, or Firm—Phillips, Moore, Lempio & Finley

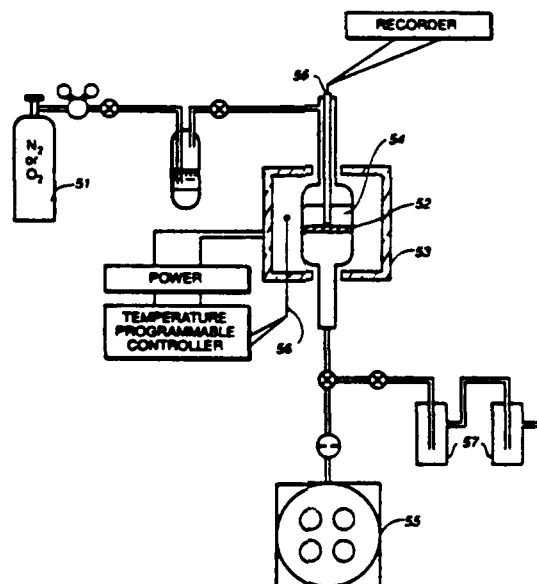
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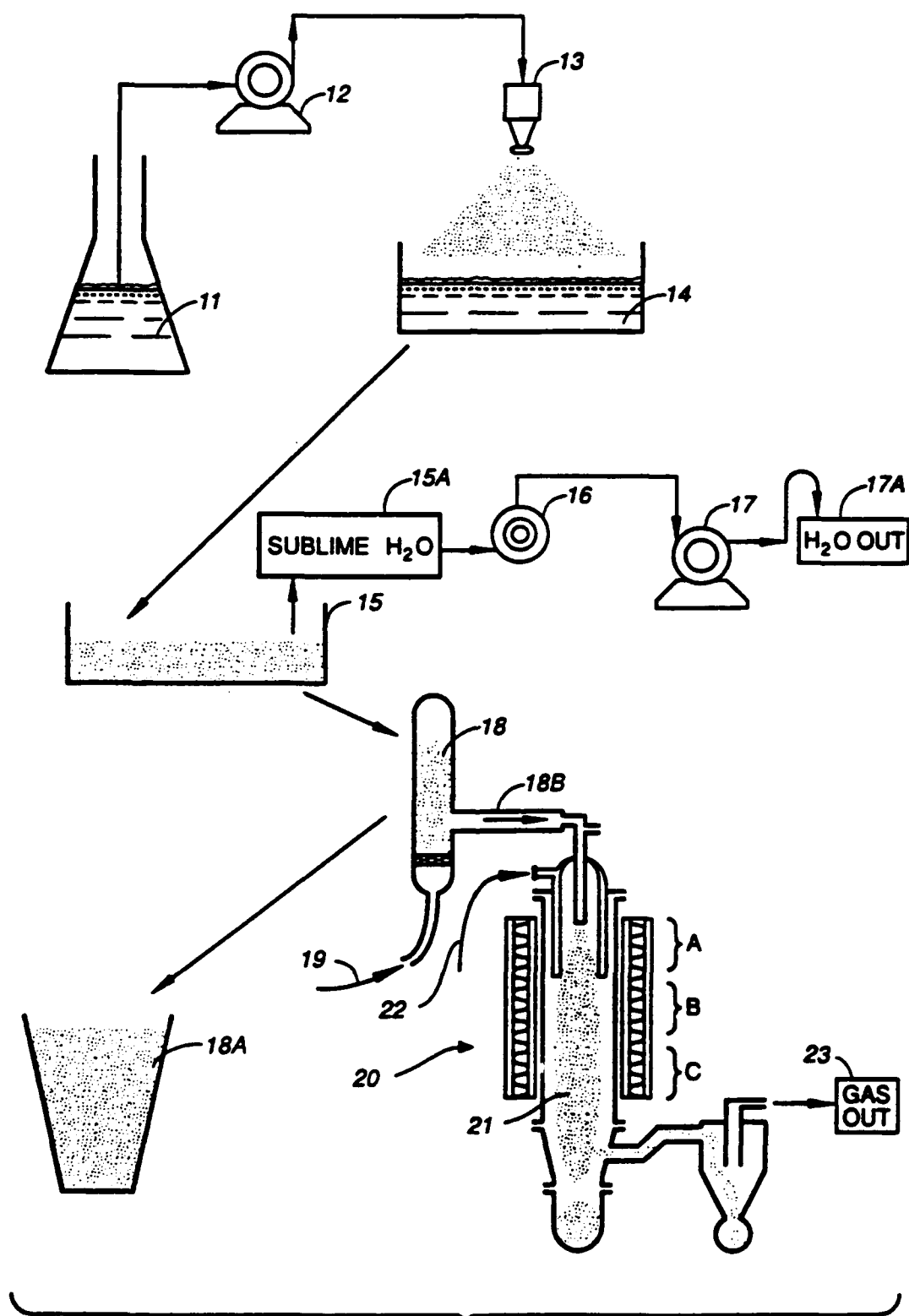
ABSTRACT

The present invention relates to an improved process to produce an essentially carbon-free nitrate of an alkali metal, alkaline earth metal, transition metal, lanthanide metal, actinide metal, metal, or mixtures thereof, which process comprises:

Contacting an anhydrous composition of an alkali metal, alkaline earth metal, transition metal, lanthanide metal, actinide metal, or mixtures thereof substituted with an organic or an inorganic carbon-containing substitute with flowing nitrogen dioxide, dinitrogen tetroxide or mixtures thereof at a temperature of between about 40° to 150° C. under anhydrous conditions for a time and at a pressure effective to form the nitrate of the alkaline metal, alkaline earth metal, transition metal, lanthanide metal, actinide metal, or mixtures thereof, essentially free of any carbon containing contaminant. Materials produced by this improved process are useful as electrical superconductors, e.g. $\text{YBa}_2\text{Cu}_3\text{O}_7$, or as high performance advanced materials, e.g. BaTiO_3 or bariumaluminosilicate.

18 Claims, 14 Drawing Sheets



**FIG. 1**

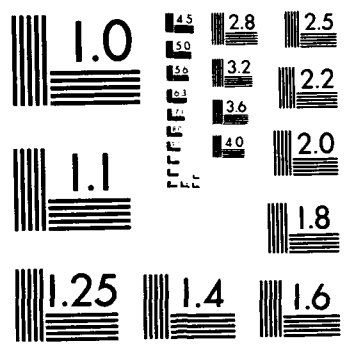
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PROCESSING AND FABRICATION OF HIGH-TEMPERATURE OXIDE
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S H JOHNSON ET AL. 30 NOV 92 XT-DARPA DARPA ORDER-9525

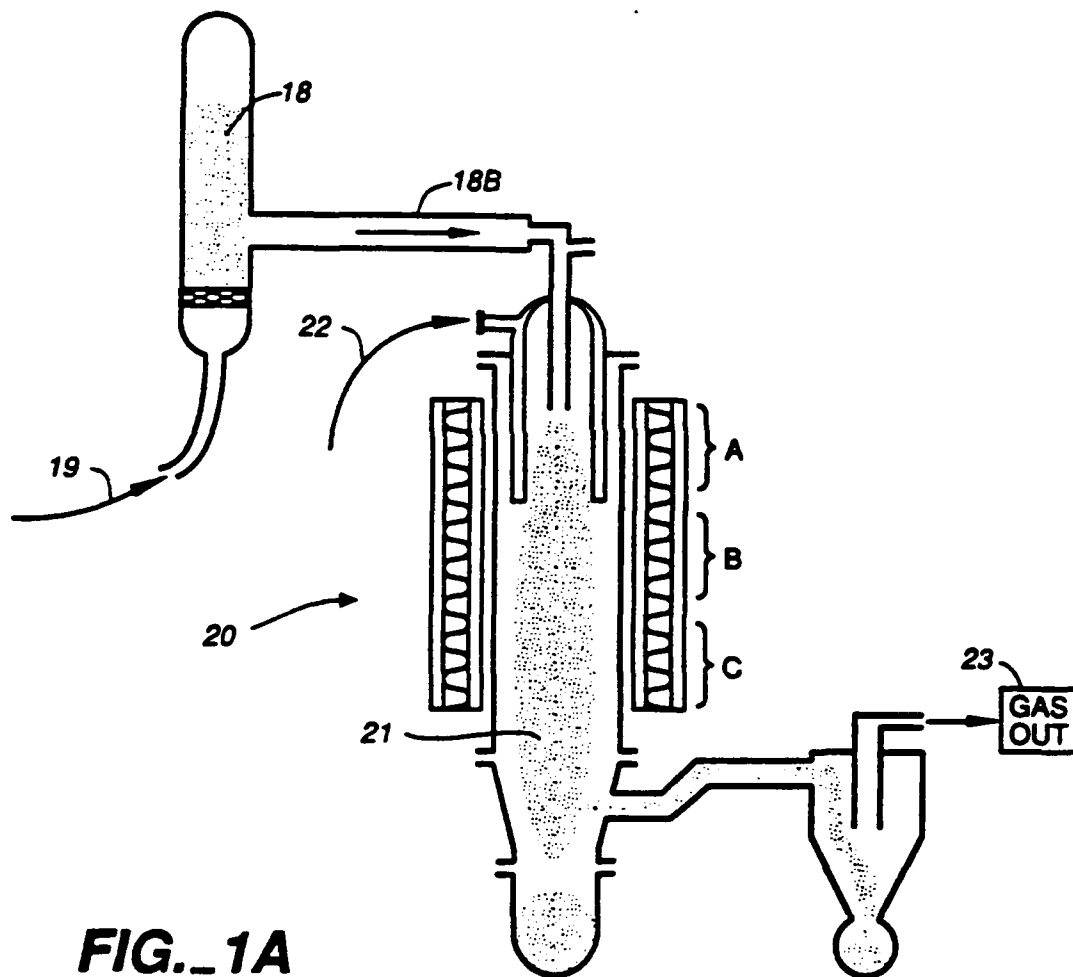
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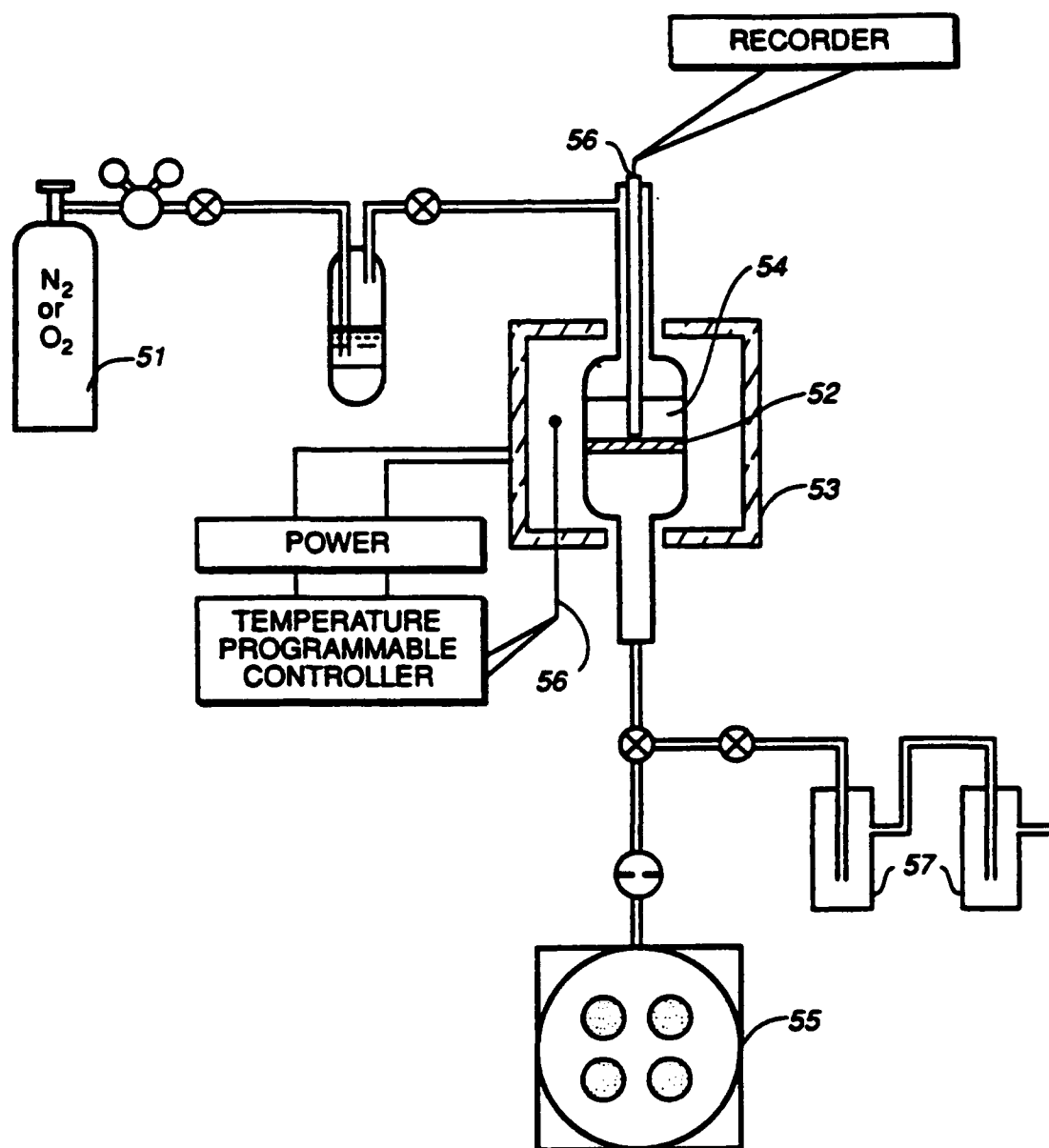
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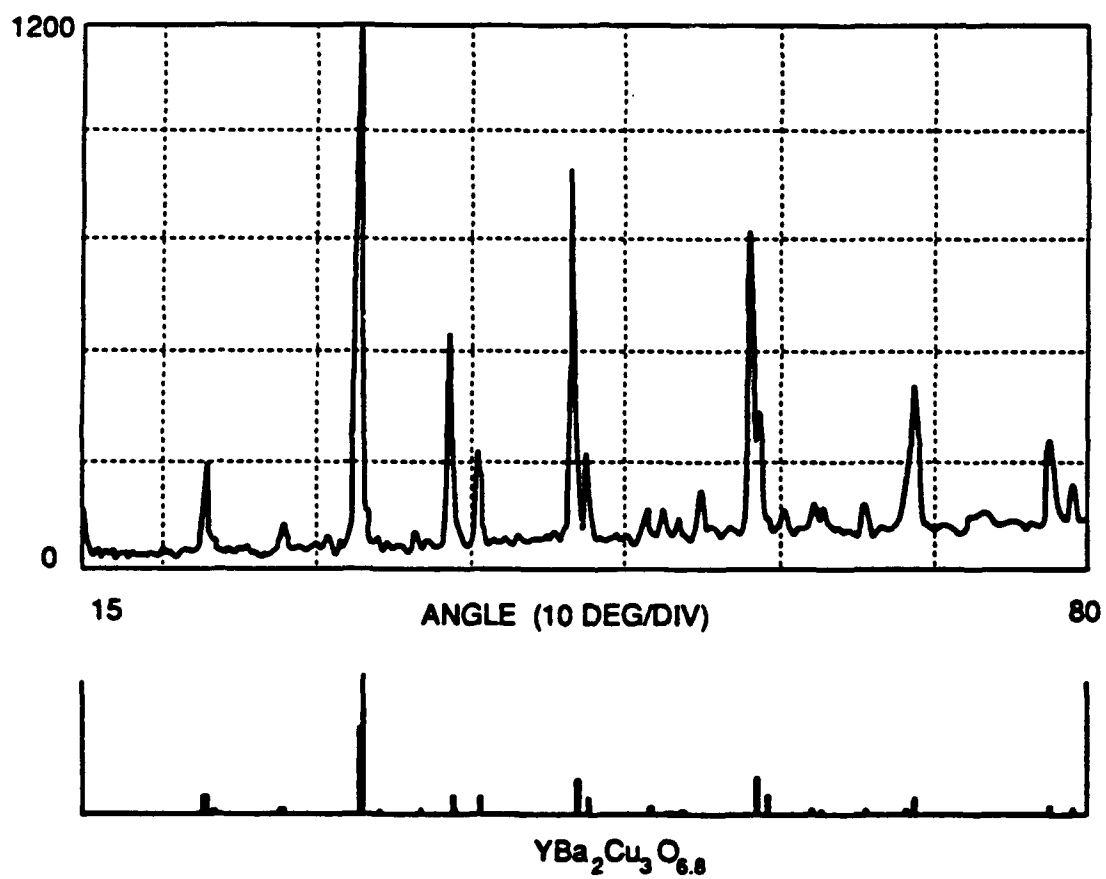
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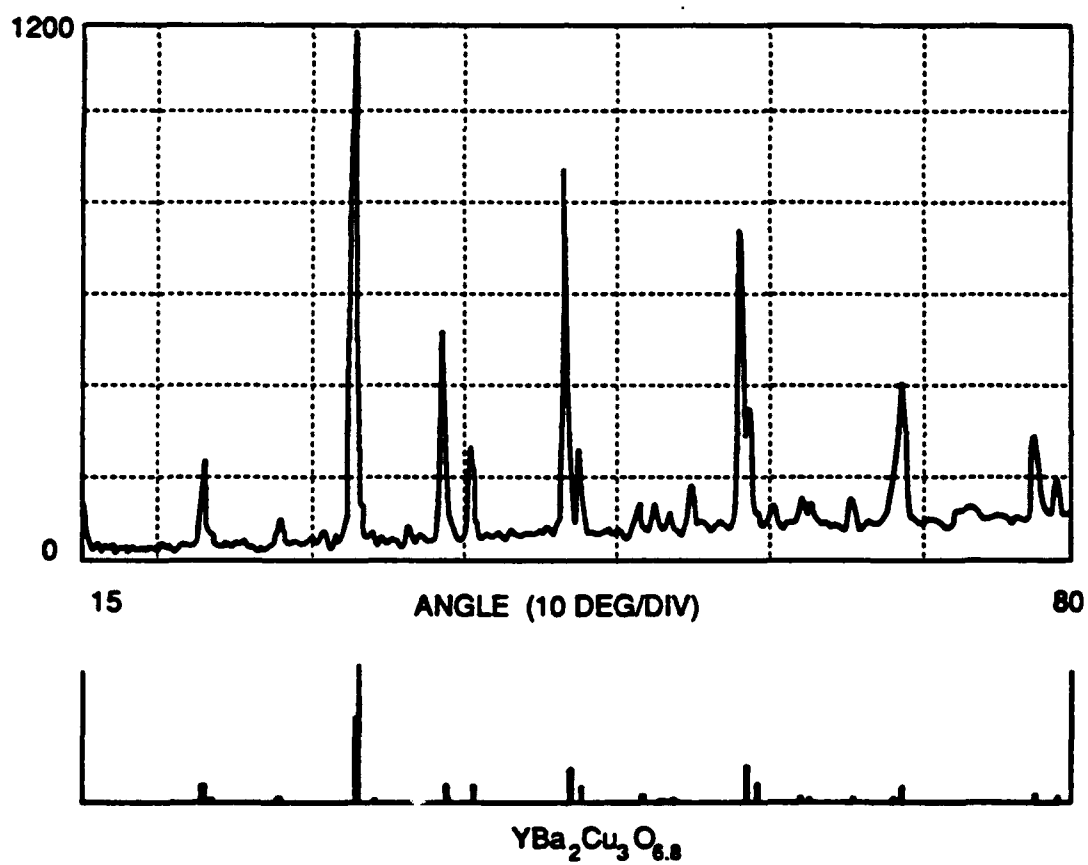


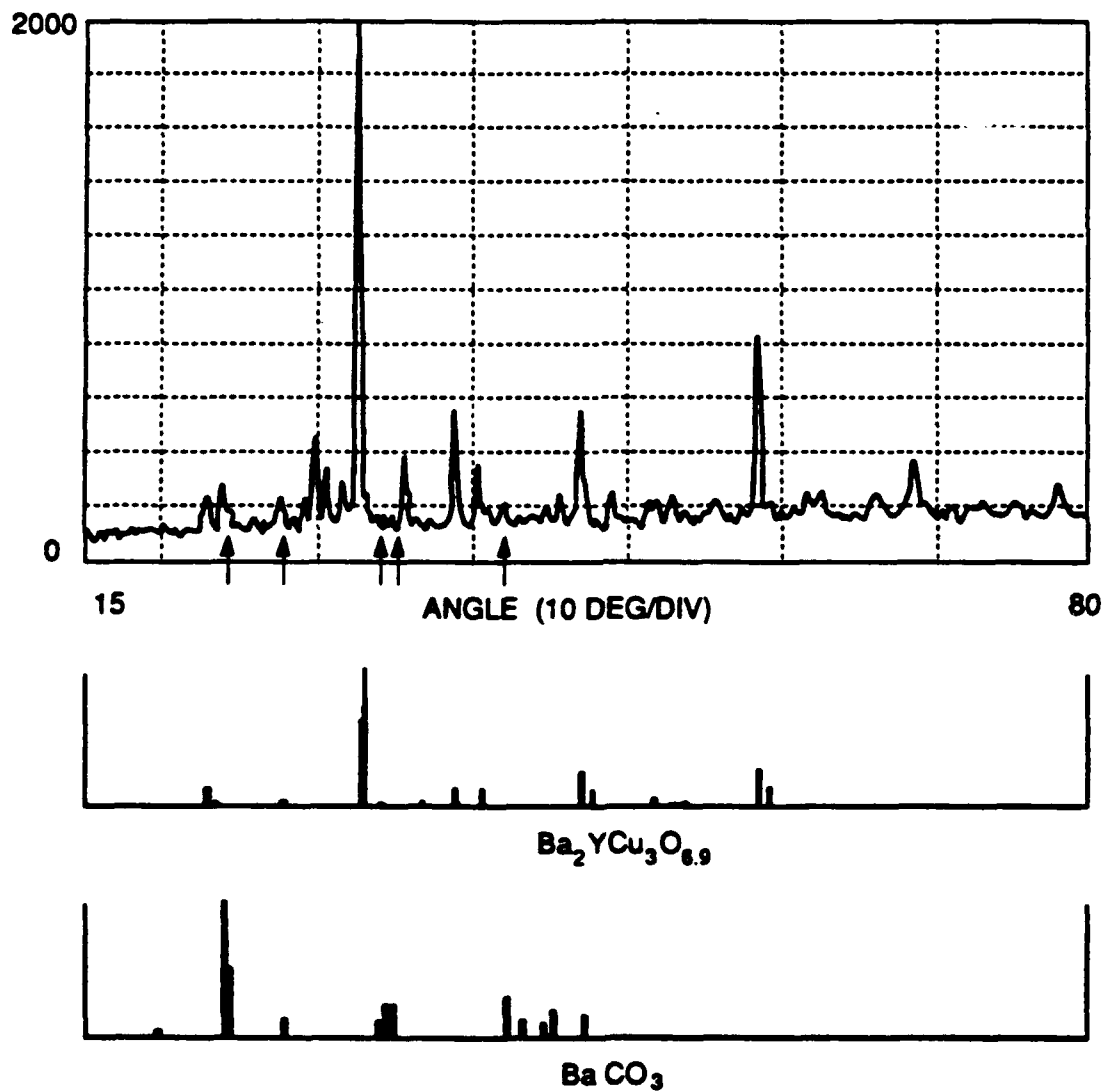
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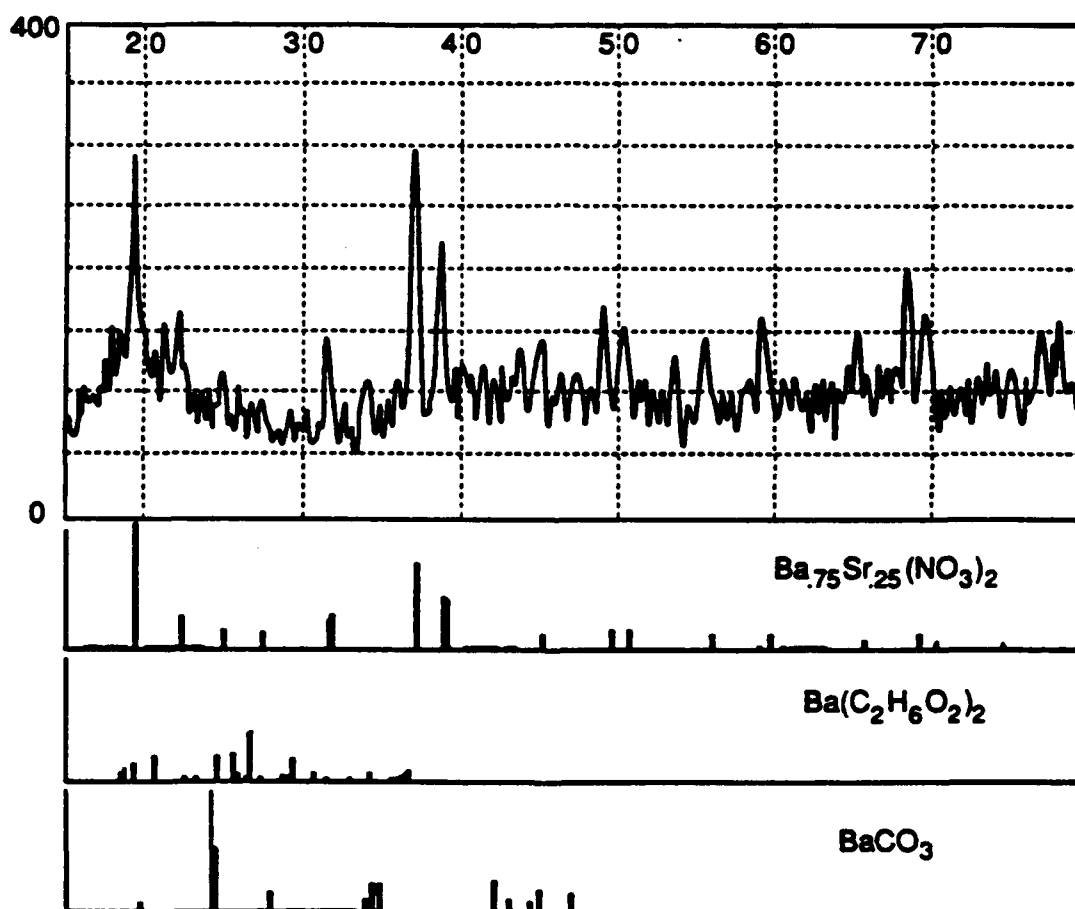
**FIG. 1A**

**FIG._2**

**FIG. 3**

**FIG. 4A**

**FIG. 4B**

**FIG. 4C**

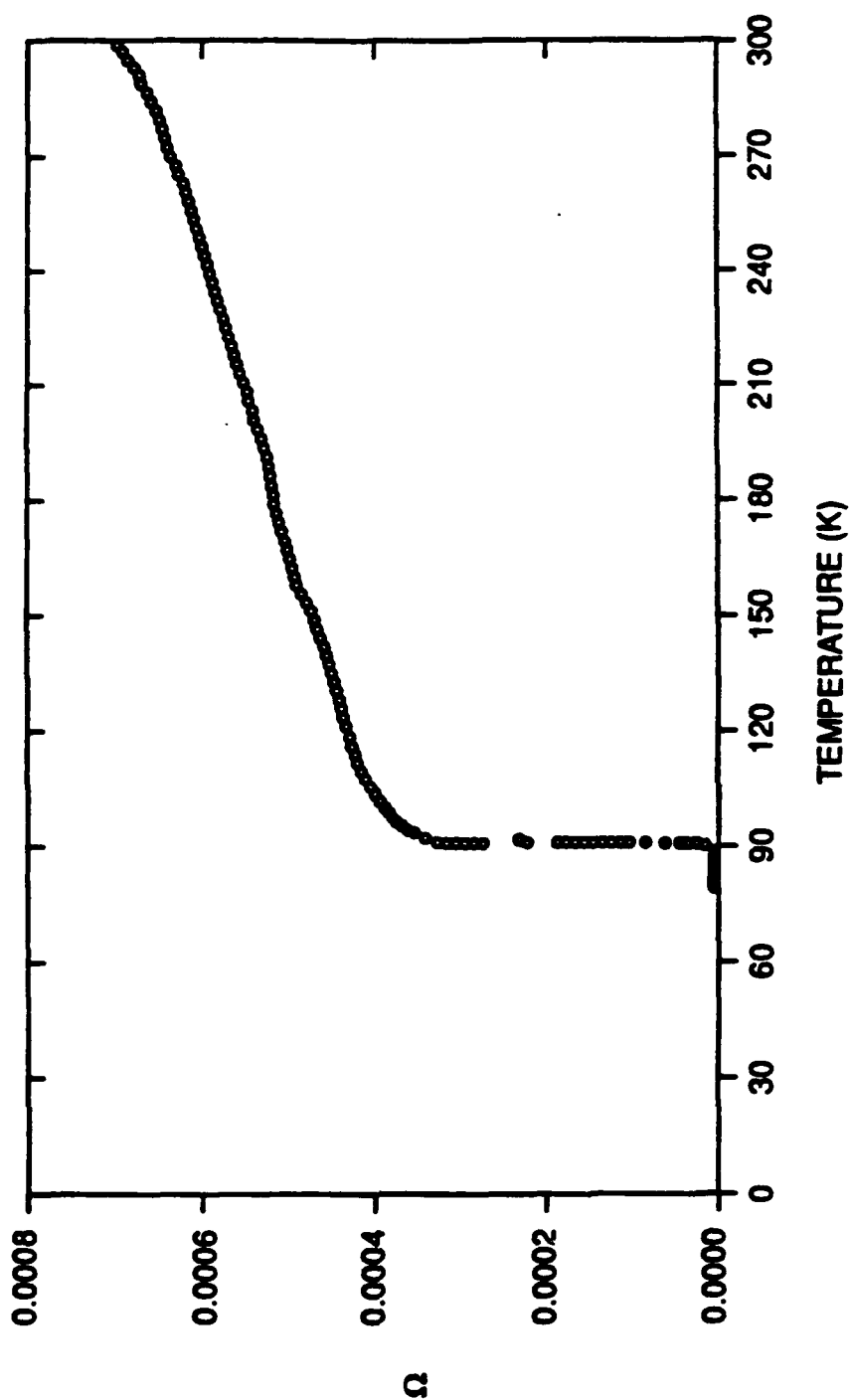
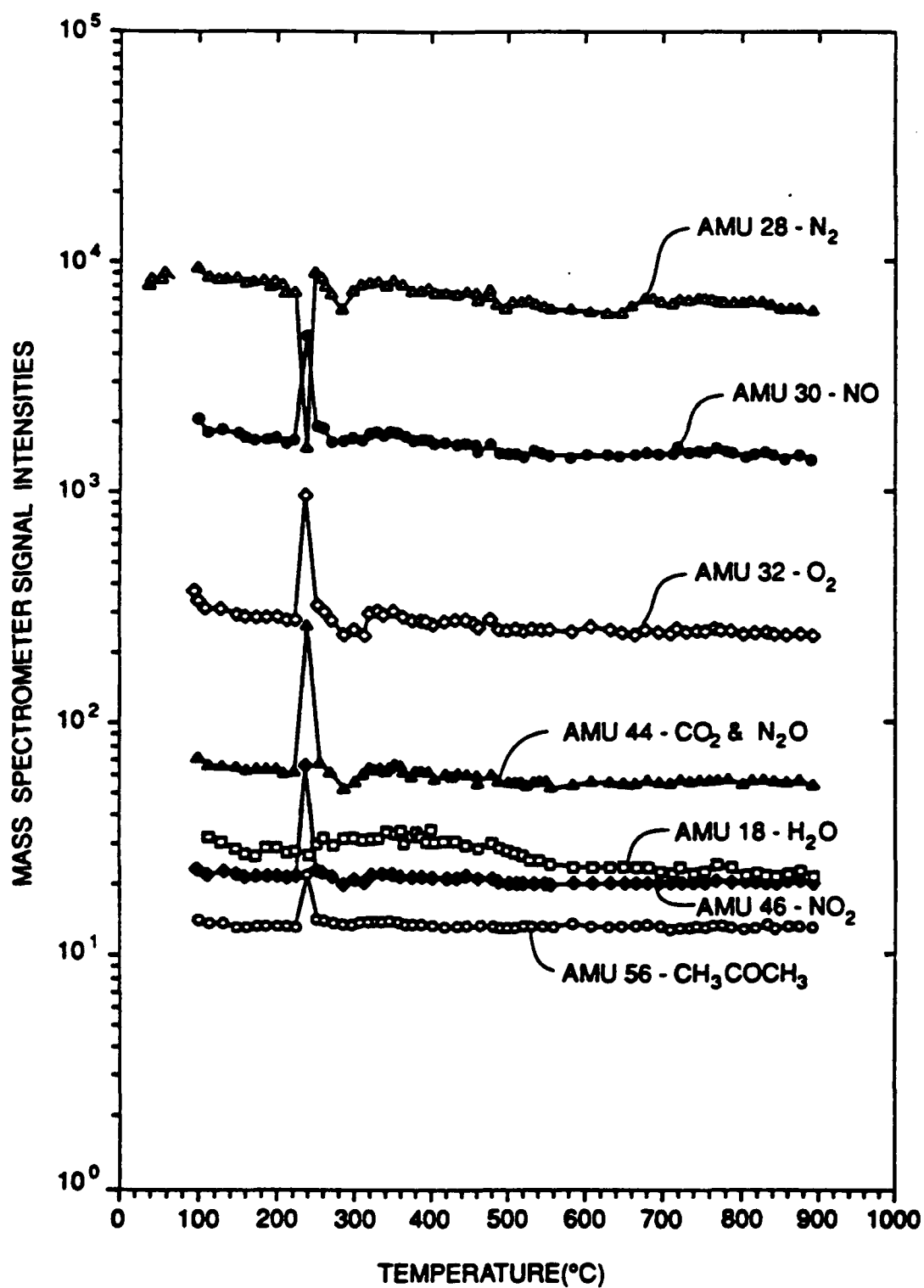
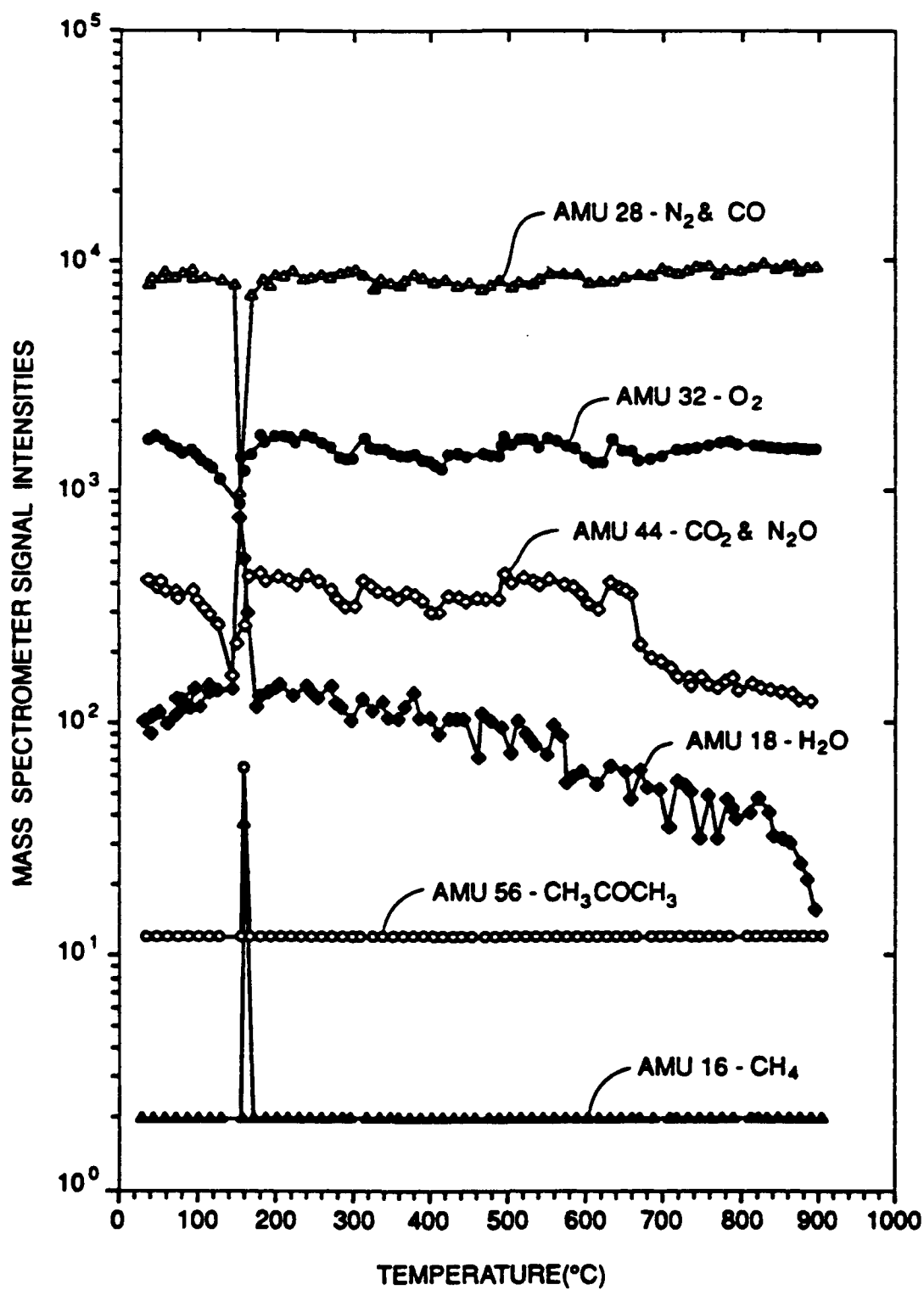
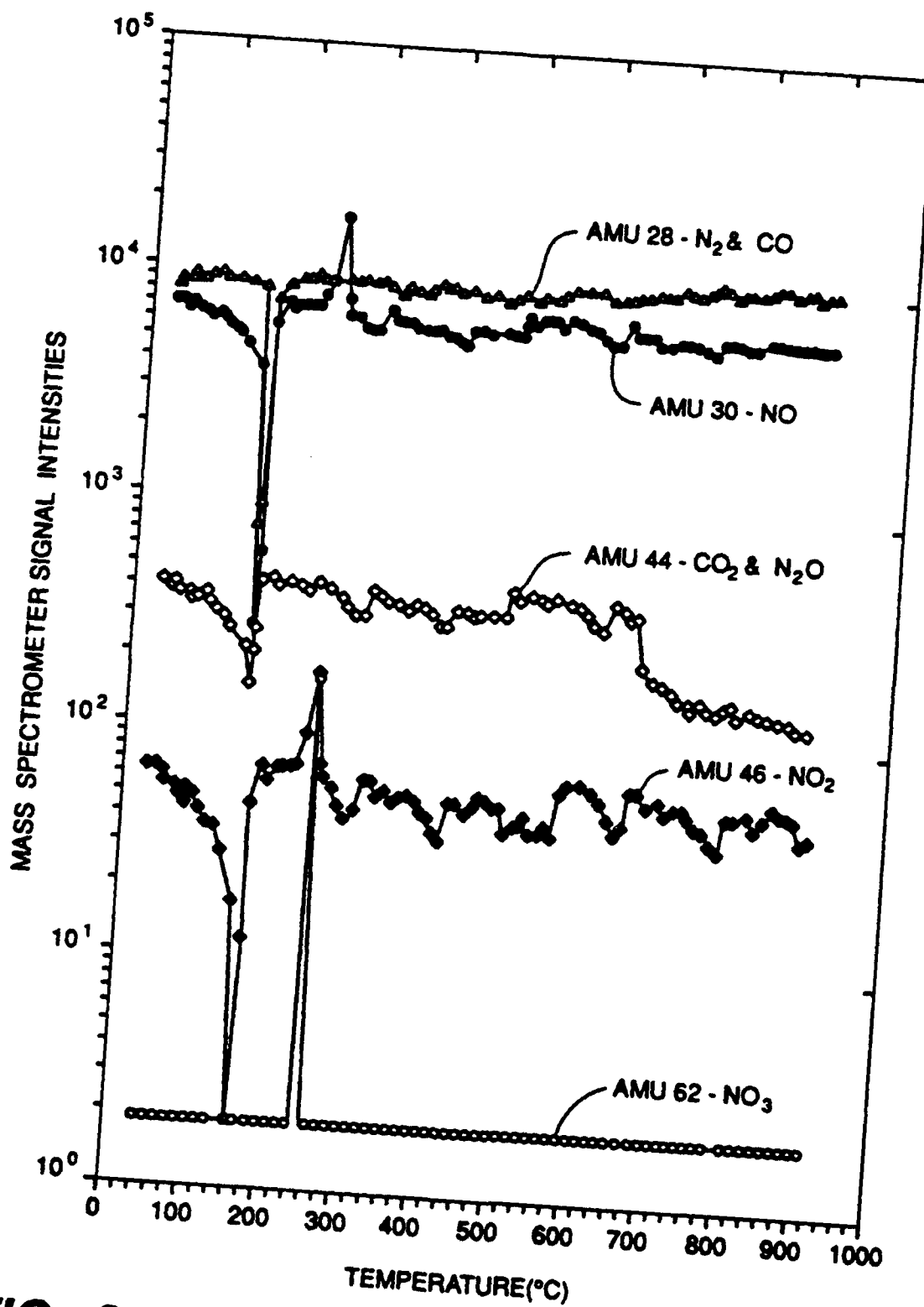
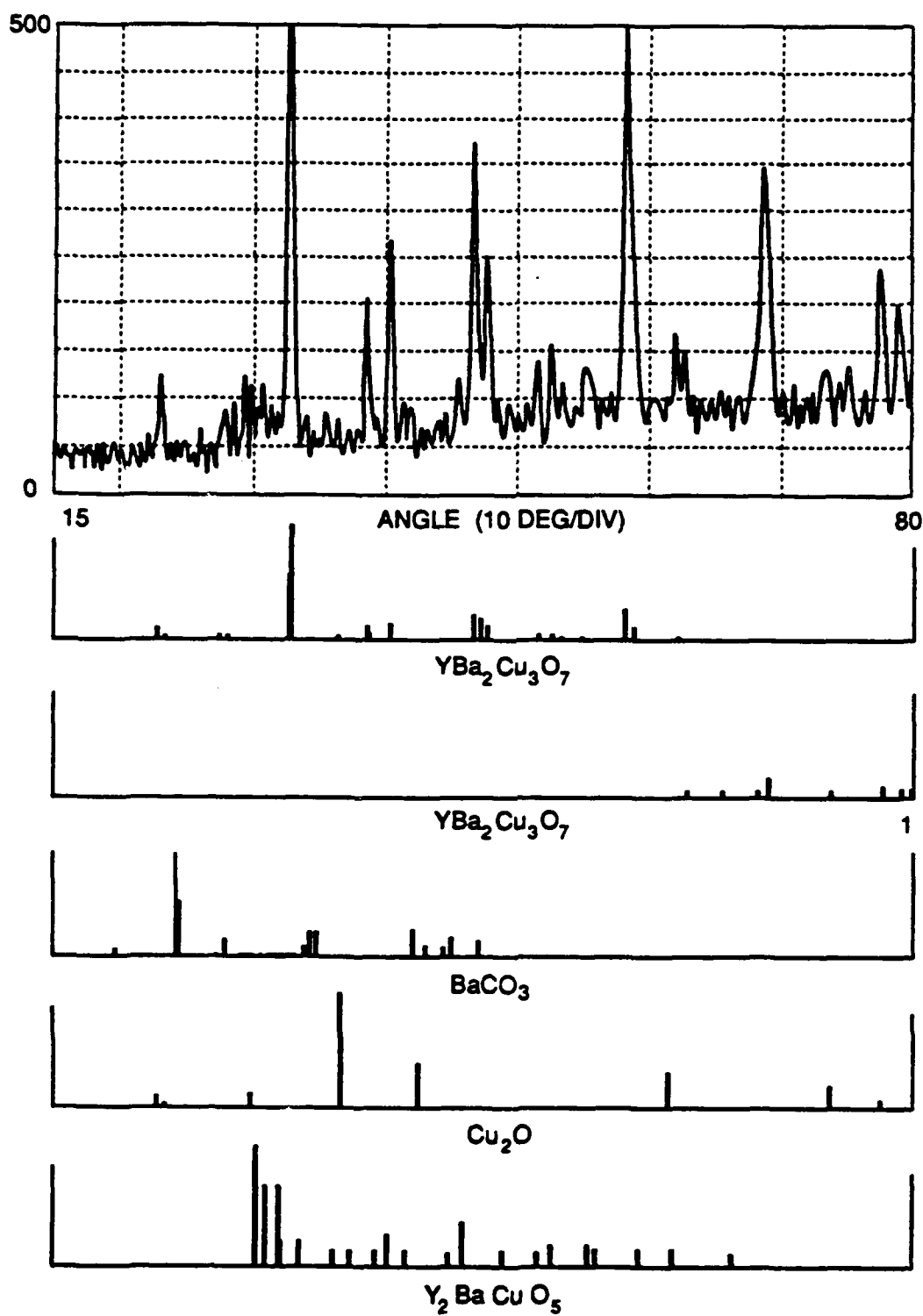


FIG. 5

**FIG. 6**

**FIG. 7**

**FIG. 8**

**FIG. 9**

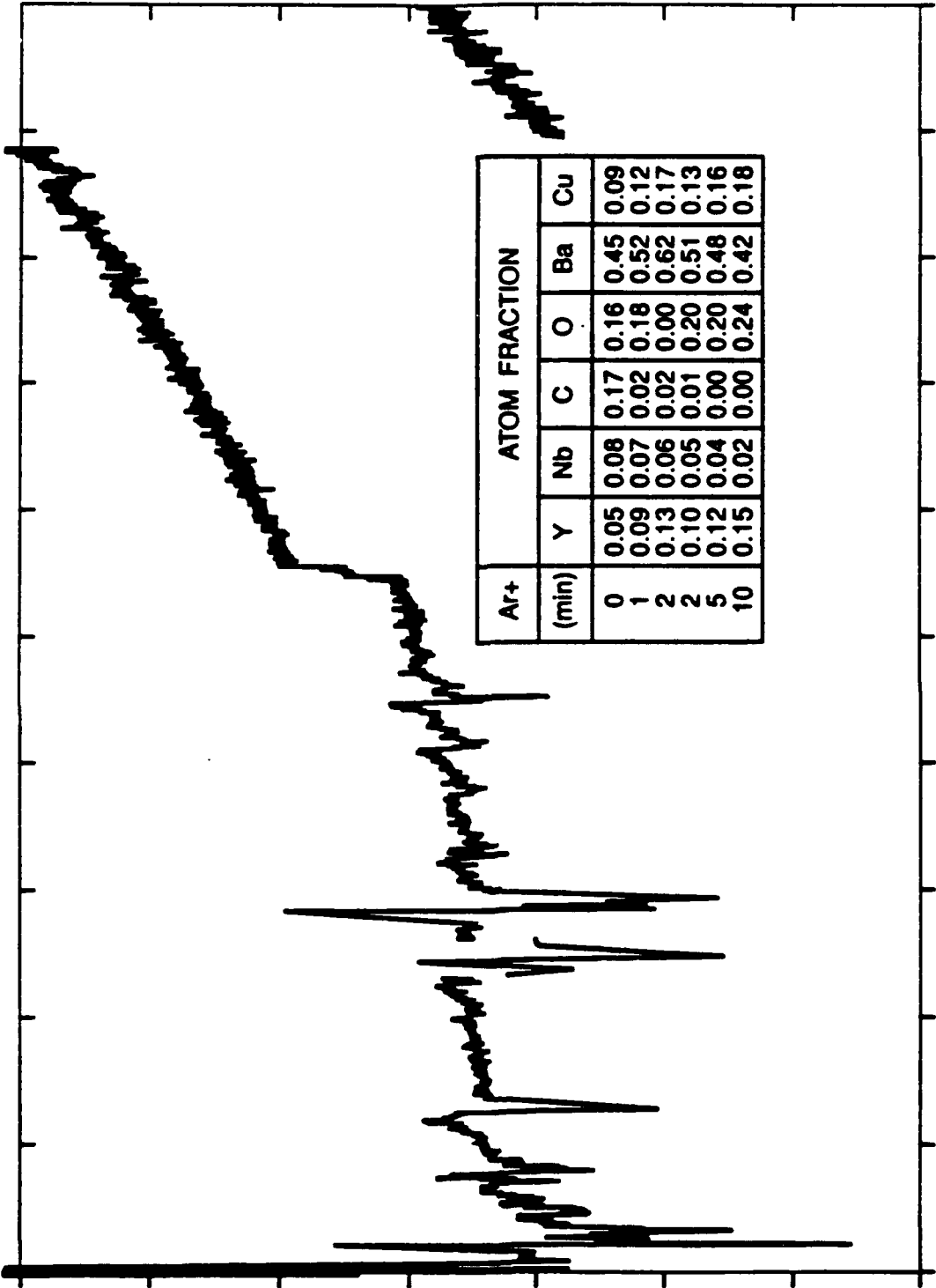


FIG.- 10

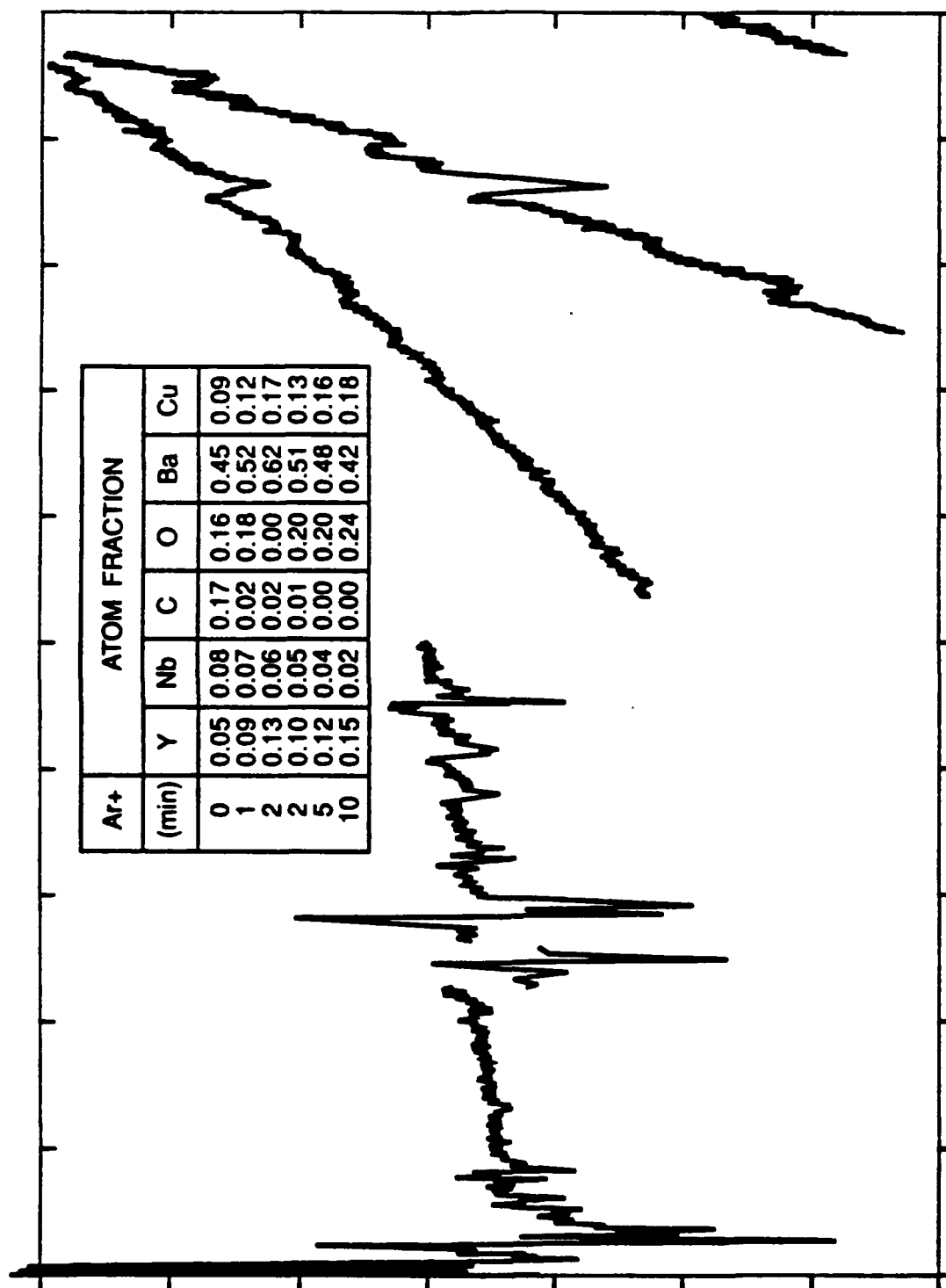


FIG. 11

CARBONATE-FREE INORGANIC NITRATES OR OXIDES AND PROCESS THEREOF

ORIGIN OF THE INVENTION

The present invention was made in the course of the Office of Naval Research Contract #N00014-88-C-0705 of the U.S. Department of Defense. The U.S. Government has certain rights in this invention.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for obtaining essentially carbon or carbonate-free inorganic nitrates or oxides. Specifically, the present invention relates to the treatment of a carbon-containing organic or inorganic salt or a mixture of salts with a nitrate-generating group, e.g., NO_2 , at essentially anhydrous conditions between about 40 and 200° C. to produce a solid carbon or carbonate-free nitrate or mixture of nitrates. The process is particularly useful to produce a mixture of oxides, e.g., $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$, (where d is between about 0 and 0.7) having high temperature (at or above 90K) electrical superconducting properties, or high performance materials, such as BaTiO_3 or barium aluminosilicate (celtsian).

2. Description of the Related Art

Various superconducting materials have been produced by processes ranging from mixing and firing oxides, nitrates and carbonates (shake and bake) (M. K. Wu et al., *Physical Rev. Letters*, Vol. 58 pg. 908 (1987)), chemical-vapor deposition (P. H. Dickinson et al., *Applied Physics*, Vol. 66, #1, p. 1 (July 1989)); sol-gel (P. Barboux et al., MRS Fall Meeting Abstracts, 1987; coprecipitation (A. M. Kini et al., *Inorganic Chemistry*, Vol. 26, Pg. 1834 (1987)); aerosol pyrolysis techniques (T. T. Kodas et al., *Applied Physical Letters*, Vol. 52 #19 pg. 1622 (1988)); or freeze drying techniques (Johnson et al., U.S. patent application Ser. No. 071,977, filed Jul. 10, 1987, now U.S. Pat. No. 4,975,415, issued Dec. 4, 1991).

K. J. Leary et al., in the *Journal of the American Ceramic Society*, Vol. 73 (#4), pg. 904-908 (April, 1990) disclose the use of nitrogen dioxide to improve the superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ (where d is between about 0 and 0.7) (also referred to herein as YBaCuO or as YBCO). However, the nitrogen dioxide is only contacted with the oxide at temperatures of 600° C. or greater for long times. Also see Leahy WO 9006598, published June 14, 1990.

R. B. Cass in U.S. Pat. No. 4,931,213 discloses the preparation of electrically-conductive titanium suboxides.

All references, patents, articles, standard, etc. cited herein are incorporated by reference in their entirety.

The production process may be fairly straight forward such as the shake and bake, or freeze drying approach or be somewhat more complex such as the sol-gel or coprecipitation. A problem encountered in the formation of barium containing superconducting oxides is that barium inorganic salts often have low water solubility. This makes it difficult to obtain proper solution concentrations for the freeze-drying technique described above. To circumvent this solubility problem, organic barium salts (acetates) are fairly water soluble and are used. However, these methods may be suspect because of the observations that the superconducting inorganic oxide may have undesired residual amounts of carbon present even after calcining, annealing and slow

cooling. The undesired carbon present in inorganic oxide powders is obtained from carbonates any or other organic carbon moieties. The carbon present in any form is believed to diminish superconducting properties. Therefore, a major problem in most bulk processes to produce a superconducting oxide, or an advanced performance material, is the necessary removal of all potentially contaminating carbon moieties.

The present process provides a nitrogen dioxide, pretreatment method to remove carbon-containing organic and carbon-containing inorganic moieties from a carbon-containing precursor, nitrate or oxide prior to sintering, calcining, slow cooling, annealing, and slow cooling to produce the carbon free oxide. These carbon-free nitrates and oxides are particularly useful to produce improved superconducting oxides or advanced materials.

SUMMARY OF THE INVENTION

The present invention relates to an improved process to produce an essentially carbon-free nitrate of an alkali metal, alkaline earth metal, transition metal, lanthanide metal, actinide metal, metal, or mixtures thereof, which process comprises:

contacting an essentially anhydrous composition of an alkali metal, alkaline earth metal, transition metal, lanthanide metal, actinide metal, metal or mixtures thereof, one or more of which metals are substituted with an organic or an inorganic carbon-containing substitute with flowing nitrogen dioxide, dinitrogen tetroxide or mixtures thereof at a temperature of between about 40° to 150° C. under essentially anhydrous conditions for a time and at a pressure effective to form the nitrate of the alkaline metal, alkaline earth metal, transition metal, lanthanide metal, actinide metal, or mixtures thereof, essentially free of any carbon containing contaminant.

The present invention relates to the production of higher T_c superconducting oxides having essentially no carbon or carbonate present by first contacting the dry powder with nitrogen dioxide, etc., followed by calcining to about 950° C., maintaining at a temperature up to about 950° C., cooling slowly, annealing, and cooling slowly to ambient temperature, all steps performed in the presence of flowing air or oxygen.

The present invention also relates to the production of inorganic high performance advanced materials having essentially no carbon or carbonate present by first contacting the carbon-containing precursor dry salt with nitrogen dioxide, etc. up to about 200° C., followed by calcining up to about 1400° C., maintaining at 1400° C., optionally slowly cooling, annealing, and slowly cooling to ambient temperature, all in the presence of flowing air or oxygen.

The present invention also relates to an improved process to produce a superconducting oxide comprising a barium oxide essentially free of barium carbonate as a contaminant, which process comprises:

contacting a solid comprising at least one barium compound which contains organic or inorganic carbon group with a nitrate-producing reagent at a temperature of between about 40° and 150° C. under essentially anhydrous conditions for a time and pressure sufficient to remove the carbon moiety present and simultaneously produce barium nitrate. The barium nitrate compound, and other compounds as dry solid are subsequently contacted with temperatures of up to 950° C. in

flowing air or oxygen, calcined, slowly cooled, annealed, and slowly cooled to ambient temperature all in the presence of flowing air or oxygen.

The present invention also relates to an improved process to produce a superconducting oxide comprising barium essentially free of barium carbonate as a contaminant, which process comprises:

(a) obtaining a superconducting oxide precursor composition containing barium chemically bonded to an organic or inorganic carbon group,

(b) contacting the solid oxide precursor with a nitrate-producing reagent at a temperature of between about 40° and 150° C. under anhydrous conditions for a time and at a pressure sufficient to remove the carbon group present and simultaneously produce barium nitrate and other inorganic nitrates;

(c) heating the precursor composition now containing barium nitrate up to between about 950° C. at a rate of between about 1°-10° C./min. in the presence of excess flowing oxygen or air;

(d) maintaining the oxide at between about 750° to 950° C. for between about 1 and 24 hours in flowing air or oxygen, and

(e) slowly cooling the oxide formed in flowing oxygen or air to about 550° C., annealing at 550° to 480° C. over 24 hours in flowing oxygen or air, and then cooling at between about 1°-10° C. min. to ambient temperature in flowing oxygen or air.

The present invention also relates to an improved method of preparing fine particles of superconducting ceramic powders, which method comprises:

(a) dissolving the soluble salts of cations in aqueous medium wherein said soluble salts comprises at least one carbon containing moiety;

(b) obtaining a substantially saturated solution of the salts and adjusting the pH to between about 4 and 7;

(c) atomizing the solution of step (b) onto liquid nitrogen at about -196° C.;

(d) removing the liquid nitrogen by evaporation of the nitrogen under reaction conditions such that the ice-salt crystals do not coalesce into larger particles;

(e) removing the ice by sublimation at reduced pressure under reaction conditions such that the residue does not melt;

(f) heating the solid residue of step (e) to 40°-° C. at reduced pressure under conditions such that the residue does not melt to produce a solid powder residue;

(f) heating the solid residue of step (e) to 40°-60° C. at ambient nitrogen dioxide, dinitrogen tetroxide or mixtures thereof at between about 40°-150° C. under anhydrous conditions for a time effective to replace the at least one carbon containing moiety by nitrate;

(g) calcining the solid residue in sufficient oxygen or air at a temperature of between about 200° and 950° C. increasing the temperature at a rate of between about 55 and 10° C./min.; and

(g') maintaining the solid residue at between about 850° and 1000° C. for between about 1 sec and 10 hours in flowing oxygen or air;

(h) cooling slowly the solid at a temperature of between about 900° C. to about 550° C. at a rate of between about 1 sec and 10° C./min. in flowing oxygen or air;

(h') annealing the solid at between 550° and 480° C. for between about 10 and 30 hours in flowing air or oxygen; and

(h'') cooling the solid from about 480° C. to ambient temperature at a rate of between about 1° and 10°

C./min. in flowing oxygen or air; and recovering the superconducting solid powder having an average diameter of between about 0.1 and 50 microns.

The present invention also relates to a process to produce a high T_c electrically superconducting article or an advanced material having improved thermal properties, which method comprises:

for the superconducting article

(A) combining

(i) at least one organic or inorganic metal salt of Group IIA element,

(ii) at least one organic or inorganic metal salt of bismuth or a Group IIIA, IIIB, IVA, VA or VB element; and

(iii) at least one organic or inorganic metal salt selected from Group IB, IIB, VIII or IVB elements; to produce an aqueous solution wherein the ratio of metal atoms in (i), (ii) (iii) is selected to produce a high T_c electrically superconducting article upon its subsequent high temperature pyrolysis in a flowing oxygen or air atmosphere;

(B) removing water present to produce a powder;

(C) contacting the solid powder with sufficient nitrate-producing reagent to replace any carbon containing group with nitrate and removing the volatile carbon containing group between 40° and 150° C. producing a mixture of nitrate salts;

(D) calcining the solid residue of step (E) in sufficient flowing oxygen or air at a temperature of between 700° and 950° C. for a time effective to produce the corresponding oxides; and

(E) slowly cooling the solid obtained at a temperature of between about 950° C. and 550° C. at a rate of between about and 10° C. per minute in excess air or oxygen;

(F) subsequently slowly annealing the mixed metal oxide obtained in flowing oxygen or air at about 500° C. to ambient temperature; and

(G) cooling the oxide at a rate of between about 1° and 10° C. per minute in flowing air or oxygen with the proviso that when a superconducting oxide is prepared the maximum temperature in steps (D) and (E) 950° C.; and

for the advanced material

(A) combining

(i) at least one metal salt of a Group IIA element,

(ii) at least one metal salt selected from bismuth or a Group IIIA, IIIB, IVA, IVB or VB element; and

(iii) optionally at least one metal salt selected from Group IB, IIB, VIII or IVB elements; to produce an aqueous solution wherein the ration of metal atoms in (i), (ii) (iii) upon its subsequent high temperature pyrolysis in a flowing oxygen or air atmosphere;

(B) removing water present to produce a solid powder;

(C) contacting the solid powder with sufficient nitrate-producing reagent to replace any carbon containing group with nitrate and removing the volatile carbon containing group between 40° and 150° C. producing a mixture of nitrate salts;

(D) calcining or sintering the solid residue of step (E) in sufficient flowing oxygen or air at a temperature of between about 500° and 1400° C. for a time effective to produce the corresponding oxides; and

(E) cooling the solid obtained at a temperature of between about 1400° C. and ambient temperature at a rate per minute to produce the advanced material in

excess air or oxygen. The material may be annealed as needed.

Preferably in the process to produce superconducting materials, the Group IIIA, IIB, IVA, VA elements are each independently selected from bismuth, lanthanum, yttrium, vanadium, praseodymium, lead, thallium, samarium, europium, gadolinium, dysprosium, holmium, terbium or mixtures thereof,

the Group IIA elements are each independently selected from barium, strontium, calcium or mixtures thereof, and

the Group IB, IIB, IVB or VIII elements are independently selected from platinum, copper, silver, tin or mixtures thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an schematic representation of one embodiment of the production of nitrate from a solid obtained using a freeze-dried process.

FIG. 1A (portion of FIG. 1) is a schematic representation of an entrained flow reaction system (fluidization) used to produce the inorganic nitrate oxide.

FIG. 2 is a schematic representation of a temperature programmed reactor (TPR) system to produce the inorganic oxides.

FIG. 3 is an x-ray diffraction pattern of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sample from a barium nitrate precursor after calcining in oxygen at 825° C. for 20 hours with no annealing in the 500° C. range.

FIG. 4A is an x-ray diffraction pattern of a similar sample of FIG. 3 which was sintered at 890° C. and annealed at 550° C. for 20 hours.

FIG. 4B is an x-ray diffraction pattern of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sample without a nitrogen dioxide pretreatment. Undesirable barium carbonate is present.

FIG. 4C is an x-ray sample of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sample pretreated with nitrogen dioxide at 110° C. for 20 minutes before calcining. No barium carbonate is present.

FIG. 5 is a plot of resistivity ($\Omega\text{-cm}$) versus temperature (K) of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ of FIG. 4C.

FIG. 6 is a plot of the mass spectral fragments of species evolved in the temperature programmed reaction of (TPR see detail below) $\text{YBa}_2\text{Cu}_3\text{O}_7$ in nitrogen only from 10° C./min. up to 900° C.

FIG. 7 is a plot of the mass spectrometer intensities of the species found in the TPR of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ precursor in nitrogen dioxide/nitrogen up to 900° C.

FIG. 8 is also a plot of the mass spectrometer intensities species generated during a TPR of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ precursor in nitrogen dioxide/nitrogen up to 900° C.

FIG. 9 is an x-ray diffraction pattern of a nitrogen dioxide/nitrogen treated $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ sample of the TPR of FIGS. 7 and 8 compared with x-ray diffraction standards.

FIG. 10 is a spectrum of YBaCuO using Auger electron spectroscopy. The spectrum shown some surface carbon present (0.17) and virtually no carbon at 12 angstroms or more within the layer.

FIG. 11 is a different spectrum of YBaCuO using Auger electron spectroscopy at a later time. The interpretation is the same as for FIG. 10.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

Definitions as used herein:

"Carbon containing inorganic compound" refers to carbonates, carbides, and the like.

"Carbon containing organic compound" includes but is not limited to acetates, propionates, butyrates, etc., tartrates, citrates, oxalates, malates, and the like.

"Continuous Process"—It is to be understood that any of the process steps described herein may be configured in a manner that a continuous stream of solid is contacted with nitrogen dioxide, dinitrogen tetroxide or mixtures, calcined, heated, cooled slowly, annealed and cooled slowly to ambient temperatures to produce purified product.

"Group IA" elements refers to lithium, sodium or potassium. Lithium is preferred. Group IA can be used in conjunction with the Group IIA elements or alone.

"Group IIA elements" refer to magnesium, calcium, strontium, barium or mixtures thereof. Barium and strontium are preferred. Barium is specially preferred.

"Group IIIB elements" refer to scandium, yttrium or any of the lanthanide elements having an atomic number of 57 to 71 or the actinide elements. Yttrium and the lanthanides from 57 to 71 are preferred. Yttrium is specially preferred.

"Group VA elements" refer to nitrogen, phosphorus, arsenic, antimony, or bismuth. Bismuth is preferred.

"Group IB elements" refer to copper, silver or gold. Copper is preferred.

"Group IIB elements" refer to zinc, cadmium or mercury. Zinc or cadmium are preferred.

"Group IIIA elements" refer to boron, aluminum, gallium, indium or thallium. Thallium is preferred for superconductors. Aluminum is preferred for advanced materials.

"Group IVA elements" refer to silicon, germanium, tin, or lead. Tin or lead are preferred.

"Group VIII elements" refer to iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium or platinum.

"Group IVB elements" refer to titanium, zirconium or hafnium. Titanium or hafnium are preferred.

"Group VB elements" refers to vanadium, niobium, tantalum. Vanadium or niobium are preferred.

"High T_c " refers to temperatures, warmer than 4° K, preferably at least 30 K. More preferably, the temperature is at or above liquid nitrogen temperatures of 77 K, preferably 90 K or warmer.

"Optionally" means that a group may or may not be present or that a particular step may or may not need to be performed within the present invention.

"Superconducting oxides" refers to a mixture of lanthanide metal, actinide metal, transition metal, alkaline earth metal, metal oxides or mixtures thereof which when properly prepared produce a perovskite or perovskite-like structure which has electrically superconducting properties at temperatures higher than 90 K.

Referring now to FIGS. 1-9, the present invention provides a process to produce metal nitrates (and therefore oxides) which are essentially carbon-free (and carbonate-free).

Superconducting Solid Oxides

The precursor solutions and solid materials are produced according to procedures known in the art, e.g. coprecipitation or freeze-drying (S. M. Johnson, et al. U.S. Ser. No. 71,977, which is specifically incorporated herein by reference.)

In the coprecipitation technique to produce precursor superconducting oxide, the acetates, citrates, oxalates, or nitrates, oxides or the like (where the metals present are originally in a proper ratio) are simply com-

bined by being poured together as aqueous solutions (usually highly concentrated). The pH is adjusted (e.g. using ammonia, ammonium hydroxide, etc.). The precursor compound precipitates and is recovered by filtration and removal of the residual water using reduced pressure. Alternatively, the water is simply removed by evaporation.

In the freeze-drying process, the saturated aqueous solutions (metals in a proper ratio) to ultimately produce a superconductor are combined and immediately spray atomized onto liquid nitrogen. The ice formed is sublimed and removed.

In the freeze drying process as shown in FIG. 1, the salt solution is optionally concentrated (or individual salt solutions which are mixed immediately, 1-5 minutes prior to) spray atomizing onto liquid nitrogen. Ultrasonic nozzles (from Sono-Tek, Poughkeepsie, N.Y.) are used, e.g., type 8700-60 (#51027). The mean droplet size is between about 15 and 50 micrometers, preferably about 30 micrometers.

The liquid nitrogen is evaporated at low temperatures, usually less than -50°C . The ice is then sublimed under controlled low temperature and vacuum conditions, e.g. less coalesce.

The precursor solid powder is then contacted with flowing nitrogen, flowing nitrogen dioxide, dinitrogen tetraoxide or mixtures thereof at about ambient temperature and then heated to between about 40°C – 150°C . The carbon-containing groups are replaced by nitrate, and the carbon-containing vapor product is removed.

Because of the carbon present in the precursor oxide the temperature of the contact with nitrogen dioxide initially must be below 200°C ., preferably 150°C . or less. If the temperature or rate of heating is too rapid, spontaneous decomposition or explosions are encountered.

The time necessary depends upon the volume present. Often one hr. or less is sufficient to remove the carbon present. The nitrates decompose cleanly to produce the corresponding desired mixture of oxides.

Bulk—The anhydrous solid is then heated at a rate of between about 1° and $10^{\circ}\text{C}/\text{min}$ to about 950°C ., in flowing oxygen or air maintained at 900° – 950°C . in flowing air or oxygen between about for 1 to 24 hours. After slow cooling at 1° – $10^{\circ}\text{C}/\text{min}$. to about 500°C . in flowing air or oxygen, the sample is annealed at about 500°C . for between about 1 to 24 hours in flowing air or oxygen, then cooled slowly at a rate of between 1° to $10^{\circ}\text{C}/\text{min}$ in flowing air or oxygen.

Analysis by x-ray diffraction analysis shows that essentially no carbon (as undesirable carbonate) is present. (FIG. 9)

Resistivity measurements ($-\text{cm}$) of the pressed powder show that the sample has superconducting properties at about 90 K and higher.

The present superconducting material produced by this nitrogen dioxide pretreatment process appears (by XRD) to be forming at temperatures lower than any yet reported (see material heated to 825°C . for 20 hours.)

Entrained Flow Reactor—As seen in FIG. 1A, the nitrates are added to the top of the reactor in flowing oxygen or air. Region A can be 800° – 1000°C . Within 1 to 5 seconds the oxides are formed and rapidly cooled (1-5 sec) in Region B to Region C to about 100°C . The oxides can then be heated to about 950°C . and cooled and annealed all in flowing oxygen or air as described herein.

An aspect of the present invention is that the superconducting powders sintered compacts produced from the show a minimum of twinning, i.e. less than 0.5%, essentially in the absence of twinning. Twinning in this art is believed to occur in the polycrystalline YBaCuO because of the strain induced in this material, by the uptake of oxygen during the transition of the material from the tetragonal phase to the superconducting orthorhombic phase. If twinning is present in these samples, it is below the detection limit of the analysis by optical micrographs taken at 1000 power.

The Auger spectra (FIG. 10 and 11) are surface measurements of the same sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ taken several days apart. A vacuum of 10-11 milli Tor is present. As can be seen, only the top layer has any minor carbon. The low carbon levels in deeper layers is at the detection level for the analysis method.

High Performance Advanced Materials

The present process is also useful to produce high purity advanced performance materials, such as BaTiO_3 or celsian, $\text{BaAl}_2\text{Si}_2\text{O}_8$. The calcining temperature is about 500°C ., and the sintering temperature maybe 1400°C . or higher.

Seeding—In additional embodiments, fine powder particles (or seeds) of an oxide compound may be suspended in the stirred precursor solutions and carried along with them as they are spray atomized into liquid nitrogen or coprecipitated. These seed particles then serve as nucleation sites to encourage the formation and growth of crystalline particles of the desired composition or phase structure. This is the case for $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ or the monoclinic structure form of celsian (barium aluminosilicate). These seeds may also influence the size and shape of particles formed from the solutions. Another use of the seed particles is to produce products with a mixed phase structure, such as BiSrCaCu oxide superconductor, as a grain boundary phase in $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$.

While not wanting to be bound by theory, it is believed that the carbonate is present in the final superconducting oxides because, as the carbon-containing metal salt is thermally decomposed, carbon dioxide is produced at the elevated temperature. This carbon dioxide combines with barium oxide present to produce the undesirable stable barium carbonate. In the present invention, the barium acetate (oxalate, etc.) is reacted with nitrogen dioxide to produce the barium nitrate. It is believed that essentially anhydrous conditions are present. However, the desired salts may have 1-9 waters of hydration, and also include up to about 0.5 percent by weight of additional water. The nitrogen dioxide probably reacts with water under the higher temperatures to produce energetic essentially pure HNO_3 in situ. The nitric acid then reacts with the salts to produce the desired nitrates.

General Experimental Description

The temperature-programmed reaction (TPR) technique (See FIG. 2) is used to characterize the reactive species in the YBaCuO freeze-dried precursor's decomposition and reaction chemistry. The reactor and process design is used to produce carbonate-free YBaCuO powder.

In one TPR experiment, a dilute stream of reactant gas is continuously passed over the sample (prepared by freeze-drying techniques) oxide precursor at a fixed rate. The sample is then heated at a known linear rate as

the reaction products are monitored by quadruple mass spectrometer (FIG. 2). A thermocouple attached to the outside of the microreactor is used as feedback for controlling the heating rate in order to avoid overheating. A thermocouple situated inside the reactor bed is used to monitor the actual reaction temperature.

A 0.5 g sample of freeze-dried precursor powder is loaded into a quartz microreactor under a nitrogen atmosphere, sealed and transferred to a TPR system.

The TPR experiments are performed at a heating rate of 1-10°/min. up to 900° C. in these different environments: N₂, O₂, NO₂/N₂, NO₂/N₂, N₂O/N₂, and NH₃/N₂.

Table 1 on the next pages shows a number of the test reaction conditions used to pretreat the superconducting oxide precursor. Run 18 using nitrogen dioxide is preferred as a test example.

TABLE 1

TPR RUN	Reactant Gases & Temperature Profile	Phases Detected in XRD Scans					
		YBCO	2-1-1	BaCO ₃	CuO	Y ₂ O ₃	Other
1	N ₂ → 100 900 500 100	VS	W	VW	Ø	Ø	M
2	N ₂ → 100 900 500 100	VS	W	W	Ø	Ø	S
3	O ₂ → 100 900 500 100	VS	VW	S	VW	W	
4	N ₂ O → 100 900 500 100	M	Ø	VS	S	Ø	
5	N ₂ /NO ₂ → 100 900 500 100	VS	W	Ø	Ø	VW	
6	NH ₃ → 100 900 500 100	Ø	Ø	S	Ø	W	VS {Cu ⁺ }
7	N ₂ /NO ₂ → 100 900 500 100	VS	W	Ø	Ø	Ø	S
8	N ₂ /N ₂ O → 100 900 500 100	VS	W	VW	VW	Ø	
9	N ₂ /HNO ₃ /H ₂ O → N ₂ O → 100 625 900 500 100	VS	W	Ø	Ø	Ø	W {Y ₂ BaO ₄ }
10	N ₂ /HNO ₃ /H ₂ O → N ₂ O → 100 625 900 500 100	Ø	Ø	Ø	M	Ø	S {Ba(NO ₃) ₂ }

TABLE 1-continued

TPR RUN	Reactant Gases & Temperature Profile	Phases Detected in XRD Scans					
		YBCO	2-1-1	BaCO ₃	CuO	Y ₂ O ₃	Other
11	NO → 100 900 500 100	M	0	VS	M	0	
12	N ₂ → N ₂ /HNO ₃ /H ₂ O → 100 325 900 500 100 N ₂ O →	VS	M	0	0	0	
13	N ₂ → N ₂ /HNO ₃ /H ₂ O → 100 325 900 500 100 N ₂ O →	VS	0	0	0	W	
14	N ₂ → N ₂ /HNO ₃ /H ₂ O → N ₂ O → 100 325 900 500 100	S	S	0	W	0	
15	NO → N ₂ O → 100 650 900 500 100	0	M	0	S	0	S
16	NO → O ₂ → 100 650 900 500 100	S	0	M	0	0	VS
17	NO → O ₂ → 100 650 900 500 100 HOLD 30 min.	VS	W	S	0	0	
18	N ₂ /1% NO ₂ → O ₂ → 100 650 900 980 500 100	VS	W	0	0	0	

Foot Notes Regarding Table 1

In Table 1 are described 18 TPR runs performed under somewhat different processing conditions. For example, Run 1 is a TPR of a YBaCuO sample in flowing nitrogen from 100° C. to 900. at a rate of heating of 10° C./min. The sample is not held at 900° C. The sample is then allowed to cool in flowing nitrogen at 5°-10° C./min. The sample is not annealed at 500° C., but is cooled in flowing nitrogen to 100° C.

The other Runs are performed in a similar manner.

Run 18 is the contacting of YBaCuO powder with flowing 1% nitrogen dioxide/nitrogen from about 100° to 900° C. at a rate of heating of 10° C./min. at 900° C. The nitrogen dioxide is topped and flowing oxygen is introduced. The rate of cooling from 900° C. to 100° C.

is a rate of 5°-10° per min. This sample produced in this run did not have carbon present.

YBaCO is YBa₂Cu₃O_{7-d}.

2-1-1 is presence of Y₂BaCuO_{7-d}.

Cu is copper oxide.

Y₂O₃ is yttrium oxide.

Other is other unidentified compounds.

0 is essentially zero.

The following Examples are provided to be illustrative and descriptive only. They are not to be construed as limiting in any way.

PREPARATION A

Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ ($d=0-1$) (without nitrogen dioxide treatment)

(a) To a 2,500-ml beaker at STP containing a magnetic stirring bar and 1000 ml of distilled water is added 66.833 g of barium acetate (0.262 mol, 99.9% purity from Johnson-Matthey of Seabrook, N.H.). Yttrium nitrate, (99.9%) 50.00g (0.131 mole) also from Johnson Matthey, in 500 ml of distilled water is added next. Next is added 100 g of copper nitrate. $3\text{H}_2\text{O}$ (0.393 mol of 99% purity), also from Johnson Matthey. The components are all in solution after heating at 90°C . for 16 hours (overnight), pH about 4. The two liters of aqueous solution are spray atomized onto 4 liters of liquid nitrogen using a thin layer chromatography spray nozzle or an ultrasonic nozzle type 8700-60 from Sono-Tek, Poughkeepsie, N.Y., over a 2.5 hr. period. The liquid ammonia is then removed by evaporation using a slight vacuum. While the ice/salt crystals are still at a very low temperature, vacuum system is attached, and the ice is sublimed at 150 mTorr. Next, the solid is allowed to heat for 4-16 hours at 40°C - 60°C . under a vacuum of 300 mTorr. The sample is immediately calcined in flowing oxygen starting at 200°C . and increasing the temperature to 895°C . over a 4 hr period. The oxides formed are then cooled in flowing oxygen (1.5 l/min.) to ambient temperature. The particles obtained have a size of between about 0.5 and 2 microns. When the oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ where d is 0-0.7, is tested for superconductivity, the oxide has a T_c of about 90 K or warmer.

(b) To obtain copper nitrate useful in step (a), pure copper metal is contacted with excess anhydrous nitric acid. The copper nitrate solution is separated, titrated to determine the concentration, and is used immediately to avoid carbon dioxide and water contamination.

(c) In one process, the copper nitrate of step (b) is combined with the yttrium nitrate and freshly prepared barium acetate. The solutions are combined, immediately mixed, and spray atomized within 5 minutes, onto liquid nitrogen to avoid carbon dioxide contamination.

EXAMPLE 1

Barium Nitrate Formation in $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$

(a) 25 Grams of freeze dried precursor composition (powder prepared in the same manner as previously described prior to calcining at 200°C . in U.S. patent application Ser. No. 71,977—Preparation A) is loaded into a quartz reactor of 1-3" diameter having a 3" height of Rashig rings (quartz) under $\frac{1}{4}$ " layer of alumina felt (or a reaction fitted with a quartz frit) to support the freeze-dried precursor powder bed. The bed is useful in height from 1-4" e.g. (1.5") before fluidization.

Dry powder is added to the reactor under an anhydrous nitrogen atmosphere because of the highly hygroscopic nature of the precursor powder.

The fluidized bed is initially fluidized using anhydrous nitrogen gas. This initial fluidization proceeds with a slow warming of the bed from 40°C . to 100°C . in the presence of nitrogen. Nitrogen dioxide is then slowly added at about 75°C . and higher to avoid exothermic reaction. The nitrogen dioxide gas is slowly introduced into the gas stream via either a NO_2 bubbler or a heated sample cylinder containing liquid NO_2 . Nitrogen dioxide concentration reaches 1-60 volume percent, (e.g. nitrogen dioxide nitrogen e.g., 25/75; V/V). The temperature of the fluidized bed is either

maintained at 100°C . or slowly raised at $2^\circ\text{C}/\text{min}$ to about 130°C . An explosive reaction can occur at about 145°C . or above if the heating rate is too fast. The displacement of the acetate groups from the barium acetate is allowed to proceed under the NO_2 gas mixture at about the elevated temperature of 110°C . for 10-30 min. After acetate removal and nitrate substitution is complete, the reactor and product is allowed to cool with either an anhydrous N_2 or NO_2/N_2 gas flow through the fluidized bed.

The cooled reactor contents are emptied under anhydrous N_2 and placed into a warm dry alumina crucible. The crucible is then placed directly into a calcining furnace preheated to 200°C - 350°C . with O_2 flowing at 0.5-1 L/min. Alternatively, the reactor contents in powder form are added directly to an entrained flow vertical reactor at 900°C . in flowing oxygen.

(b) The oxides of subpart (a) are heated at 850°C to 950°C . for 1-4 hours and cooled slowly at 1°C - 10°C . per minute in flowing oxygen or air to 550°C ., annealed from 550°C to 480°C . over 24 hours and cooled at 1°C - $10^\circ\text{C}/\text{min}$ to ambient temperature. A useful superconducting oxide powder is obtained.

Barium Titanate

(c) Barium titanate (BaTiO_3) is formed as described in Example 1 (a) and 1(b) above except that the spray solutions contain the required amounts of $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ and titanium n-butoxide as the reactants to produce this oxide. The calcining and maintained temperature in Example 1(b) is up to 1400°C .

Celsan

(d) Barium aluminosilicate Celsan is formed as described in Example 1(a) and 1(b) above except the spray solutions contain the required amounts of $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, silicon tetraethyl orthosilicate or colloidal silica, and aluminum n-propionate as the reactants. Seeds of monoclinic celsan may be included in the spray atomization to encourage the growth of the desired monoclinic crystal structure. The calcining and maintained temperature in step 1(b) is up to 1400°C .

EXAMPLE 2

Coprecipitation

(a) The procedure of Example 1 is repeated except that the dry $\text{YBa}_2\text{Cu}_3\text{O}_7$ precursor powder is obtained by coprecipitation of the appropriate salts followed by removal of the water by evaporation or sublimation of the water present.

EXAMPLE 3

Barium Titanate

The procedure of Example 1 is repeated except that barium acetate and titanium nitrate are present in the ratio necessary to ultimately produce BaTiO_3 . The calcining and heating temperature is also up to 1400°C . for 10 hours. The special cooling and annealing steps are not necessary. Barium titanite essentially free of carbon impurity having improved thermal properties is obtained.

EXAMPLE 4

Barium Aluminosilicate

The procedure of Example 3 is repeated except that acetate and aluminum nitrate $0.9\text{H}_2\text{O}$ and silicon tetraethyl orthosilicate are each originally present in a ratio to ultimately produce $\text{BaAl}_2\text{Si}_2\text{O}_x$ essentially free of carbon contaminant having improved thermal properties. Special cooling of annealing steps are optional.

While only a few embodiments of the invention have been shown and described herein, it will become apparent to those skilled in the art that various modifications and changes can be made in the process to produce essentially carbon-free inorganic oxide powders which are useful as superconducting oxides or other advanced materials without departing from the spirit and scope of the present invention. All such modifications and changes coming within the scope of the appended claims are intended to be carried out thereby.

We claim:

1. An improved process to produce an essentially carbon-free nitrate independently selected from an alkali metal, alkaline earth metal, transition metal, lanthanide metal actinide metal, or mixtures thereof, which process comprises:
 - contacting an essentially anhydrous composition of an alkali metal, alkaline earth metal, transition metal, lanthanum metal, actinide metal, or mixtures thereof at least one of which are substituted with an organic or an inorganic carbon-containing substituent;
 - with flowing nitrogen dioxide, dinitrogen tetroxide or mixtures thereof at a temperature of between about 100° to 150° C. under essentially anhydrous conditions for a time and at a pressure effective to remove carbon the group present and to form the nitrate of the alkaline metal, alkaline earth metal, transition metal, lanthanide metal, actinide metal, or mixtures thereof essentially free of any carbon containing contaminant wherein the composition is the combination of lanthanide metal, alkaline earth metal and transition metal present in a ratio to each other to produce an electrically superconducting oxide, upon subsequent processing.
2. The process of claim 1 wherein the carbon-free nitrate compounds comprise yttrium, barium and copper.
3. An improved process to produce a superconducting oxide comprising barium essentially free of barium carbonate as a contaminant, which process comprises:
 - (a) obtaining a superconducting oxide precursor composition containing barium chemically bonded to an organic or inorganic carbon group,
 - (b) contacting the oxide precursor with a nitrate-producing reagent at a temperature of between about 100° and 150° C. under anhydrous conditions for a time and at a pressure sufficient to remove the carbon group present and simultaneously produce barium nitrate and other inorganic nitrogen containing compounds,
 - (c) heating the precursor composition now containing barium nitrate up to 950° C. at a rate of between about 1° - 10° C./min. in the presence of excess flowing oxygen or air; and
 - (d) maintaining the oxide at 950° C. for between about 1 and 6 hours,
 - (e) slowly cooling the oxide formed in flowing oxygen or air to about 550° C., annealing at 550° to

480° C. over 24 hours and cooling at 1 - 10° C. min. to ambient temperature.

4. The process of claim 3 wherein the superconducting oxide precursor of step (a) comprises

- (i) barium acetate, barium propionate, barium citrate, barium oxalate, barium tartrate or mixtures thereof;
- (ii) lanthanum nitrate, yttrium nitrate or mixtures thereof; and
- (iii) copper nitrate.

5. The process of claim 4 wherein the superconducting oxide precursor comprises barium acetate, yttrium nitrate and copper nitrate; the nitrate-producing reagent is nitrogen dioxide present in 1-60 percent in an inert gas and the contact time is up to 59 minutes.

6. An improved process of preparing fine particles of superconducting ceramic powders, which method comprises:

- (a) dissolving the soluble salts of cations in aqueous medium wherein said soluble salts comprises at least one carbon containing moiety;
- (b) obtaining a substantially saturated solution of the salts and adjusting the pH to between about 4 and 7;
- (c) atomizing the solution of step (b) onto liquid nitrogen at about -196° C.;
- (d) removing the liquid nitrogen by evaporation of the nitrogen under reaction conditions such that the ice-salt crystals do not coalesce into larger particles;
- (e) removing the ice by sublimation at reduced pressure under reaction conditions such that the residue does not melt;
- (f) heating the solid residue of step (e) at 40° - 60° C. at reduced pressure under reaction conditions such that the residue does not melt to produce a solid powder residue;
- (f') contacting said solid powder residue with sufficient nitrogen dioxide, dinitrogen tetroxide or mixtures thereof at between about 100° - 150° C. under anhydrous conditions for a time effective to replace the at least one carbon-containing moiety by nitrate;
- (g) calcining the solid residue in sufficient flowing oxygen or air at temperature of between about 200° and 895° C. at a rate of between about 1° and 10° C./min.; and
- (g') maintaining the solid residue at between about 850° and 900° C. for between about 0.001-10 hours in flowing oxygen or air;
- (h) cooling slowly the solid at a temperature of between about 900° C. to about 550° C. at a rate of between about 1° and 10° C./min. in flowing oxygen or air;
- (h') annealing the solid at between 550° and 480° C. for between about 10 and 30 hours in flowing oxygen or air; and
- (h'') cooling the solid from about 480° C. to ambient temperature at a rate of between about 1° and 10° C./min. in flowing oxygen or air; and
- (i) recovering the superconducting solid powder having an average diameter of between about 0.1 and 50 microns.

7. The process of claim 6 wherein in substep (b) the pH of about 4 to 7 of the aqueous solution is obtained by treating the aqueous medium with ammonia or ammonium hydroxide.

8. The process of claim 6 wherein the particles have a spinel, perovskite, or perovskite-like structure comprising:



wherein:

A and A' are each independently selected from lanthanum, yttrium, samarium, europium, gadolinium, dysprosium, holmium or mixtures thereof;

B and B' are each independently selected from barium, strontium-calcium, barium-strontium or barium-calcium;

D is selected from platinum, copper, silver, tin or mixtures thereof;

x is about 1;

y is about 2;

z is about 3; and

q is 7-d, where d is between 0 and 0.7.

9. The process of claim 6 wherein in step (b) the pH is between about 4 and 5.

10. The process of claim 6 wherein step (a) the soluble salts are selected from organic and inorganic salts.

11. The method of claim 10 wherein in step (a) the soluble salts are selected from nitrates or acetates.

12. The process of claim 10 wherein the concentration of soluble salts is between about 0.015 and 0.15 molal.

13. The process of claim 12 wherein A and A' are each yttrium.

14. The process of claim 13 wherein D is copper.

15. The process of claim 14 wherein B and B' are each barium.

16. A process to produce a high T_c electrically superconducting article, which method comprises:

(A) for the superconducting article combining

(i) at least one unsaturated organic acid metal salt of at Group IIA element,

(ii) at least one unsaturated organic acid metal salt of bismuth or a Group IIIA, IIIB, IVA, or VA element; and

(iii) at least one unsaturated organic acid metal salt selected from Group IB, IIB, VIII or IVB elements; to produce an aqueous solution wherein

the ratio of metal atoms in (i), (ii) (iii) is selected to produce a high T_c electrically superconducting article upon its subsequent high temperature pyrolysis in a flowing oxygen or air atmosphere;

(B) removing water present to produce a powder;

(C) contacting the solid powder with sufficient nitrate-producing reagent at a temperature of between about 100°-150° C. under anhydrous conditions to replace any carbon containing group with nitrate and removing the volatile carbon containing group producing a mixture of nitrate salts;

(D) calcining the solid residue of step (C) in sufficient flowing oxygen or air at a temperature of between 700° and 1200° C. for a time effective to produce the corresponding oxides; and

(E) slowly cooling the solid obtained at a temperature of between about 1200° C. and 550° C. at a rate of between about and 10° C. per minute in excess air or oxygen;

(F) subsequently slowly annealing the mixed metal oxide obtained in flowing oxygen or air at about 500° C. to ambient temperature; and

(G) cooling the oxide to a rate of between about 1 and 10° C. per minute in flowing air or oxygen with the proviso that when a superconducting oxide is prepared the maximum temperature in steps (D) and (E) is about 950° C.

17. The process of claim 16 wherein

the Group IIIA, IIIB, IVA, VA elements are such independently selected from bismuth, lanthanum, yttrium, praseodymium, lead, thallium, samarium, europium, gadolinium, dysprosium, holmium, terbium or mixtures thereof,

the Group IIA elements are each independently selected from barium, strontium, calcium or mixtures thereof, and

the Group IB, IIB, IVB or VIII elements are independently selected from platinum, copper, silver, tin or mixtures thereof.

18. The process of claim 17 wherein the maximum calcining and heating temperature is 950° C. and the superconducting oxide produced is $YBa_2Cu_3O_{7-d}$.

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