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Preparation and Properties of Y-124 Superconductor made by a Chemical Precipitation Method * CONF-900944--37

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Abstract

We have prepared the thermodynamically stable YBCO-124 high temperature superconductor in powder form by a chemical precipitation method and have characterized the material by a number of chemical and physical methods, including carbon content, x-ray diffraction, thermogravimetry, scanning electron microscopy, surface area, thermally stimulated luminescence, and the superconducting transition and magnetization curves. We have also started to consolidate the powders by hot pressing.

1. Introduction

The only problem with bulk high temperature superconductors is their limited current carrying capacity. This deficiency is generally attributed to "weak links" at the grain boundaries and to the crystalline anisotropy of the grains. The obvious remedy is to remove and/or neutralize the grain boundaries by growing larger grains and by texturing the material, i.e. aligning the grains. The difficulty with this approach, however, is that the temperatures and pressures necessary to produce texturing can also lead to decomposition of the superconductor, with the creation of non-superconducting impurity phases, which then act as weak links. Clearly, we need to use superconductors that are more stable.

The yttrium-barium-cuprate high temperature superconductor with the composition $YBa_2Cu_3O_8$ (Y-124) was first seen by Zandbergen *et al.* [1] as a defect in partially decomposed Y-123 material and has since been synthesized in high pressure autoclaves by Karpinski *et al.* [2] and by Morris *et al.* [3]. Since 124 does not undergo the tetragonal-orthorhombic phase change and since it has a fixed oxygen content of exactly 8 atoms, it should be more stable than the widely studied 123, with its variable oxygen stoichiometry of (7-6).

The high pressure syntheses of 124 require equipment that is not readily scaled to production quantities. Published pressure-temperature phase diagrams [4] [5] [6] give conflicting results for the more easily manageable and safer pressure region below 1 MPa, but it is clear that for each temperature there is a minimum permissible pressure to assure the 124 equilibrium composition, rather than 247 or 123.

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A number of recent publications report "essentially" phase-pure 124, or Ca substituted 124. [7] [8] [9] [10] [11] [12] [13]. All except one, [8] limit synthesis temperatures to 800 or 815 C and operate at or below atmospheric pressure. Most also use conventional mix-and-grind ceramic techniques with long annealing times to insure homogeneity.

The present investigation is based on material prepared by a chemical co-precipitation technique [14] and has used vacuum, [15] as well as "mild" pressure (up to 7 bar) calcinations in flowing oxygen to prepare Y-124 in 10 to 100 g lots. Co-precipitation should permit closer control of composition and homogeneity than the more conventional techniques and the subsequent compound formation should take place at lower temperatures. A possible disadvantage of "chem-prep" materials may be their fine particle size and greater susceptibility to surface contamination.

2. Powder Preparation

Superconductive Components, Inc. (SCI) has been manufacturing "standard" Y-123 under a license to use the patented process developed at Sandia National Laboratory by Bunker *et al.* [14]. The process mixes and precipitates in an ultrasonic horn aqueous solutions in tetramethylammoniumhydroxide (TMAOH) of the cations and of carbonate ion at controlled pH, and can be adapted to make Y-124 precursor by simply changing the copper concentration. The subsequent calcination of the intimately mixed hydroxides and/or carbonates of Y, Ba, and Cu includes removal of residual TMAOH by pyrolysis. This should be done as quickly as possible, to avoid the reduction of CuO to Cu by the organic material and to avoid the possible segregation of the intimately mixed elements. On the other hand, there is the requirement to completely (and slowly) decompose all carbonates, at temperatures only slightly above the pyrolysis region.

Initial batches were processed by "flash" calcination, i.e. the precursor slurry was directly introduced into the hot furnace. Subsequent batches were either pressure or vacuum calcined at different heating rates and temperatures. Our best powders still contain some carbon and the optimization of the heating protocol remains to be worked out.

It should be noted that the exact nature of the intermediate phases and the kinetics of their conversions are largely unknown in the 123 as well as in the 124 (and 247) systems. Most work on ternary phase diagrams has been done at temperatures above 850 C. Our results confirm the observations of Balachandran *et al.* [9] that, in order to form 124 rather than 123, a short "nucleating" excursion to 800 C in 1 bar of O₂, followed by an ≈24 hr reaction at 750 C is necessary, and that a subsequent "finishing" treatment at 800 C (in O₂) will improve phase purity. However, it is not yet clear whether the oxygen-vacuum CO₂ removal is necessary for our sub-micron powders. Treatments above 800 C require elevated oxygen pressures.

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3. Materials Characterization

Our aim is to control purity to better than 0.5 volume percent. Quantitative materials characterization and quality control therefore become the *sine qua non* of our endeavor. Available analytical techniques fall into three groups:

- a) Primarily chemical procedures that measure the elemental composition of a sample,
- b) Standard physical, materials science, or metallurgical methods that show the structure and morphology at the macroscopic, microscopic and atomic levels, and
- c) Specialized cryogenic techniques that define and elucidate the superconducting properties.

The equipment, expertise and manpower to apply all of these can only be mustered through the cooperative effort of a number of organizations.

3.1. Chemical Techniques

An accurate knowledge of the chemical composition of the manufactured superconductor is necessary, but not sufficient, to determine its stoichiometry. Basic Wet Chemistry techniques involve only modest equipment costs, but are time consuming, if accuracies of 1 part in 1000 are attempted. For YBCO, copper has to be removed quantitatively by Electrodeposition, before yttrium and barium can be obtained by EDTA titration.

Quicker instrumental methods for elemental analysis, such as Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES), or X-ray Fluorescence (XRF), only give accuracies of 3% at best, but are useful for trace impurities. Oxygen analysis by Iodometry [16] is, unfortunately, model dependent and indirect, since it involves separate titrations to differentiate between copper atoms of valence +2 and +3.

Carbon content, or residual carbonates, are easily measured to trace levels by the LECO method developed for the steel industry, as included in ASTM Standard E-350. [17] Carbon can also be seen with great sensitivity by Thermal Decomposition Mass Spectroscopy (TDMS) of a 50 mg heated sample through the appearance of CO and CO₂.

Insulating impurities within 1 μm of the surface can be detected with high sensitivity by Thermally Stimulated Luminescence (TSL), a technique developed at LANL. [18]

3.2. Physical Measurements

ThermoGravimetric Analysis (TGA) stands out among standard techniques in producing highly informative results, both for analysis and for guiding manufacture. The only limitation is on the magnitude of the gas (oxygen) pressure the instrument can tolerate. TGA clearly distinguishes between 123, 124 and 247 and can furnish quantitative data for 2-phase mixtures. It also shows the desorption of moisture and the decomposition of carbonates.

X-Ray Diffraction (XRD) can only find impurities above the 5 to 10 % level. Low Angle XRD must be used to differentiate between similar compounds with large unit cells, such as 123, 124 and 247, where many of the strongest lines overlap. Precision Lattice Constant (PLC) analysis of the diffraction lines may indicate subtle distortions in the crystal structure, related to the manufacturing process or to oxygen deficiency.

Electron Microscopy, both Scanning (SEM) and Transmission (TEM), can give exquisite pictures of individual grains and other morphological features. *In situ* chemical analysis of small regions during SEM or TEM by x-ray fluorescence is also possible, but only for concentrations above 5 or 10 %. Identification of individual crystallites by electron diffraction can be done in TEM.

The BET (Brunauer-Emmett-Teller) [19] surface area method can give an average particle size, but we need to know more about particle size distribution and shape.

3.3. Cryophysical Measurements

The measurements of the unique electrical and magnetic properties of superconductors furnish the essential check on the quality of our product and fall into three categories:

- a) Low field (< 10 mT) magnetic susceptibility, as a function of temperature under dc, ac, or rf conditions,
- b) Full field (0 to 5 T) magnetization, hysteresis and implicit intra-granular critical current densities, and
- c) Transport critical current densities as a function of temperature and magnetic field.

Magnetometers -- The MPMS (Magnetic Property Measuring System), based on the SQUID has been the mainstay of our work, as it is in many studies on high temperature superconductors. Its resolution, precision and accuracy are outstanding, but, for other than the discovery of new superconductors, as much as four orders of magnitude in sensitivity may not be needed and, although fully automated, even the simplest study will take hours. A Vibrating Sample Magnetometer (VSM) can make similar measurements at a faster rate and with somewhat lower sensitivity, and Integrating Coil magnetometers could be assembled from components and would be faster yet.

AC Susceptibility and Loss equipment is available both in the low frequency (10 to 100 Hz) and radio frequency (MHz) range. It can provide information about structural heterogeneity, but is mostly used to qualitatively indicate the transition and its width, rather the amount of superconducting phase.

Resistivity and Transport Critical Current Density -- For high current measurements, the temperature ranges accessible with common cryogenic liquids are severely limited. Few installations have such equipment available inside a high field magnet at other than liquid nitrogen and helium temperatures. One way around this limitation is to generate Induced Persistent Currents in hollow cylindrical structures. This method avoids contact and lead heating problems and, therefore, only needs a variable-temperature flow-cryostat inside a high field magnet.

Surface Resistivity -- Unique information about weak link behavior is obtained from a technique, developed in part at LANL, where the change in the Q of a 3 GHz TM₀₁₀ niobium cavity (with a flat 0.5 to 1 cm² specimen insert) is measured while the rf magnetic field is increased from 10⁻⁴ to 10⁻¹ Oe. Similar measurements can be made over an extended temperature range in a 28 GHz copper cavity cooled by a refrigerator, but require samples of 3.8 cm diameter.

4. Properties of Powders

We first discuss separately for each group of calcinations, the measurements that primarily guided the development of that group: the superconducting transition, XRD and SEM. We then cover TGA, BET, critical current density and other results, which cut across and unify the groups.

4.1. Flash Calcinations

The four flash calcined batches that were investigated in detail, were part of a larger set, prepared at SCI, where the gaseous environment (air or oxygen), the temperature (750, 800, 850 or 900 C), and the calcining times (4 or 10 hrs) were varied. The importance of the kinetics of the intermediate phase transformations is emphasized by the fact that none of the samples gave a clear indication of 124.

Even so, the work served as an introduction to the capabilities and limitations of the various techniques. Onsets of the transition at 92 K indicated the presence of Y-123; a strong Curie-Weiss, $1/(T-\theta)$, paramagnetic rise in susceptibility with decreasing temperature suggested unreacted CuO or Cu_2O . X-Ray Diffraction showed BaCO_3 for all calcinations under 850 C, and CuO in all samples except the 900 C one. It also showed some form of YBCO in most samples, but we could not differentiate between 123, 124, and 247.

4.2. Pressure Calcinations

The main variables studied were processing time and temperature, with the pressure selected so that the reaction would occur in the 124 region of the phase diagram. We also varied heating rates, holding times and the important step of nucleation at elevated temperatures, prior to the formation of 124 at 750 C, as suggested in the ANL vacuum processing studies. The hazards of handling oxygen gas in a ceramic tube at elevated pressures and temperatures were reduced by installing a pressure switch to shut off the throttled oxygen supply in case of a tube failure.

The first sample (355L) was taken directly to its reaction temperature of 825 C and held there for 14 hrs at an absolute pressure of 3 bar. Its transition curves still have an onset temperature of 92 K, indicating the presence of 123, but also have a second major drop at 82 or 83 K, as expected for 124. The transition is broad and shows no leveling or completion, even at 7 K. We tend to ascribe the broadening primarily to the extreme fineness of our powders, but the presence of Y-247 may also contribute.

SEM shows platelets with major dimensions of 2 μm and less. We estimate the thickness of the platelets to be no more than 200 nm, which would give a large demagnetization factor.

X-Ray diffraction. The complete set of Y-124 lines, for 2 θ angles between 20 and 60°, is observed in this first batch. The insulating Y-211 phase is also seen, plus some CuO and, possibly, Y_2O_3 . There are "bumps" at 27.15 and 31.65°, that could be attributed to the [108] and [10.12] lines of 247, but none that are unambiguously assignable to 123. Nevertheless, the presence of 123 is quite likely, since the batch had not been given the nucleation treatment, and, indeed, strongly suggested by the by the previously mentioned 92 K onset and by the TGA data on mass loss as a function of temperature.

The transition curves for the second batch (355N), Fig. 1, confirm the importance of a higher temperature nucleation, prior to 750 C reaction, to get rid of 123. The batch was "finished" for 48 hrs at 830 C in oxygen at 5 bar. The transition has a clean onset at 83 or 82 K for all measuring fields. There is a hint of a paramagnetic rise in the 20 Oe curve below 20 K.

X-Ray diffraction patterns of this and subsequent batches were done at twice the earlier resolution and over an extended 2 θ range from 5 to 74°. We can now distinguish seven weaker lines, attributable to 247, and identify Cu_2O and, possibly, Y_2O_3 and CuO , but no 123. The presence of the high-temperature, reduced form of copper oxide, Cu_2O , is unexpected.

The final pressure calcined batch (355O), was nucleated at 800 C, prior to the 750 C reaction and then finished at 840 C and 6 bar for 31 hours. It gave sharper and better resolved diffraction peaks than the samples finished at lower temperatures. It contains about the same amount of 211, but only one third as much Cu_2O . Its transition was only measured on a cold pressed cylinder. It has an onset at 83 K and has not leveled off at 7 K.

4.3. Vacuum Calcinations

Three vacuum calcinations were done by SCI in cooperation with and at the Argonne National Laboratory. The vacuum process was originally developed at ANL to improve the removal of CO_2 in ceramic process 123.[15] It was subsequently adapted to

Fig. 1. Effect of Measuring Field on Apparent Width and Magnitude of Zero-Field-Cooled Transition of Pressure Calcined Material (355N) - No demagnetization correction applied.

124, pioneering the 800 C nucleation step, and eventually to our chem-prep materials. It is evident that the process for 124 has undergone successful improvements, with the earlier samples containing paramagnetic impurities and having an onset temperature above 90 K. Also a finishing treatment, typically 24 hours in flowing oxygen at atmospheric pressure and 800 C, is clearly needed to improve the phase purity of the 124 compound.

A first sample, treated at 750 C without prior nucleation, had an onset temperature of 90 K, a very broad transition and a steeply rising paramagnetic tail below 25 K. Nevertheless, initial magnetization measurements up to 320 Oe at 7 K gave a typical superconducting pattern, as impure 123 would. The next sample, also without the nucleation, turned out to be a mixture of 123 and 124 from x-ray, transition and TGA indications.

The final sample (430B), given the full nucleation and finishing treatment at 800 C, has a clean transition, starting at 82 K. The transition is broad, shows no leveling and indicates a large demagnetization. All of this is reasonable for an assembly of very small platelets that are barely resolved at an SEM magnification of 30,000X, Fig. 2. These facts also correlate with the broader, less sharp x-ray lines, compared to samples that were finished at higher temperatures and pressures. There are clearly identifiable 247 lines, but no copper oxide.

Fig. 2. SEM for Vacuum Processed Material (430B) at Magnification of 30,000X (430B).

4.4. Thermogravimetry

Morris *et al.* [3] and Karpinski *et al.* [4] have pointed out that TGA differentiates between 123, 124 and 247, with great sensitivity. 123 starts to lose oxygen at 400 C and has lost 1.2 % of its mass at 800 C, even in an oxygen atmosphere, whereas pure 124 has lost only 0.07 % of its mass at that temperature and 247 is in between with a loss of 0.44 %. The 700 C losses are 0.9, 0.3 and 0.03 % for 123, 247 and 124, respectively.

From the mass loss TGA data of Fig. 3, we can estimate the 247 content, assuming that the absence of a 92 K onset can be used to exclude 123. Depending on the chosen reference temperature, our best 124 samples still contain 10 ± 5 % of 247.

4.5. Thermal Decomposition Mass Spectroscopy

TDMS was run in batch mode on three samples. Moisture peaks between 150 and 250 C, but continues to be evolved from the system all the way to 700 C. Carbon monoxide and dioxide usually run parallel and seem to have double peaks at about 200 and 400 C. The curves are reproduced in Fig. 4 for two of the samples. The areas under the curves scale roughly as the carbon obtained from combustion, but our method of normalizing the data to the mass of material placed in the spectrometer still needs verification.

4.6. Carbon Analyses

Preliminary carbon analyses gave 0.05 % for one of our pressure calcined samples (355-O) and 0.03 % for two of the ANL vacuum calcined samples. These numbers correspond to $BaCO_3$ contents of 0.8 and 0.5 %, respectively.

4.7. Surface Area

The results from the BET surface area determinations, obtained at a commercial laboratory, ranged from $4.5 \text{ m}^2/\text{gm}$ for the pressure calcined 355-O to $90 \text{ m}^2/\text{gm}$ for the vacuum calcined 430-B. The corresponding diameters of uniform spherical particles would be 220 and 12 nm. The former is in reasonable agreement with the SEM observations, but the values 12 or 16 nm (for 355-N) will need to be verified by alternative techniques that provide information on particle shape and size distribution. Nevertheless, there appears to be a trend in that the smallest surface areas go with the highest finishing temperatures.

4.8. Magnetization and Critical Current Densities

Magnetization-Hysteresis curves were obtained for most of the pressure and vacuum calcined powders at 10 and 40 K. The hysteretic width of the magnetization curve is commonly used to calculate an intragranular critical current density according to the Bean [20] critical state model and the relation: $J_c = 30 \Delta M / 2r$, where J_c is in A/cm^2 , ΔM the width in emu/cm^3 or Gauss, and $2r$ the particle diameter in cm.

Surprisingly, the hysteresis widths vary by less than a factor of two for the fine pressure calcined powder (355N), Fig. 5, a cylinder cold pressed from it, a coarser powder (355O), and the extremely fine vacuum calcined powder (430B).

On the other hand, in view of the uncertainties in particle size and shape discussed in the preceding section, the intragranular current densities, indicated by the tabbed numbers on the right, could be in error by an order of magnitude in either direction. Nevertheless, the indicated critical current densities, although close to the depairing limit, are not unreasonable, especially if it should turn out that 247 or possible byproducts from the transformations between the different YBCO phases provide flux pinning sites, as suggested by Morris *et al.* [5] and by Jin *et al.* [21]

Fig. 3 Comparison of TGA Observations with Literature Data [4]. Note that only the early sample (355L), which was not given the 800 C nucleation and still had a 92 K onset, is clearly outside the 247-124 region.

Fig. 4. Thermal Decomposition Mass Spectroscopy Results for the Evolution of Carbon Monoxide (solid lines) and Dioxide (dashed lines). Heavy lines are for ANL vacuum calcined batch (430B), light lines for cPa pressure finished batch (355O).

Fig. 5. Magnetization Width and Intragranular Critical Current Density as a Function of Field (0-5 T) and at 10, 20, 40 and 60 K for Cylinder Cold Pressed from Fine, Pressure-Calcined Powder (355N). Assumed particle diameter of 160nm to calculate J_c .

4.9. Precision Lattice Constants

With powder x-ray diffraction data of sufficient accuracy, lattice constants can be calculated, provided the structure is sufficiently well known. Our results agree reasonably well with the literature. All the data, including the literature ones, suggest that the c-axis parameter decreases as the maximum processing temperature is raised, but there could be other factors, such as impurity content or oxygen deficiencies.

5. Properties of Consolidated Materials

Hot pressing ceramic superconductors requires that they be protected from de-oxygenation and from reaction with the container or supports. Of eight hot pressing attempts, only two have yielded materials suitable for further examination.

The first sample to be examined in any detail, was a hard, black 25 mm diameter disk, pressed at 800 C and 1000 bar for 30 minutes. It had a coppery surface sheen, but only gave a very small diamagnetic signal with a 25 K transition temperature. We believe that it was severely de-oxygenated, primarily from contact with its mild steel holder. A small piece would start to take up oxygen in the TGA apparatus at 350 C and, after cycling to 820 C, end up with a mass gain of 0.19 %. This re-oxygenation raises the transition onset to about 40 K.

A more successful run (designated HP-8) was made at 810 C and 500 bar, using starting powder from the thoroughly characterized, vacuum calcined batch 430B. The resulting material is not fully consolidated, but consists of flakes with a slate-like morphology and dimensions of up to 15 mm.

The dc transition, measured with a 10 Oe field perpendicular to the plane of the flakes, shows a slow onset at 82 K, with the main drop below 50 K, Fig. 6. The susceptibility at 7 K exhibits the largest negative value, or demagnetization, observed in our study. Clearly, the material is very anisotropic.

The rf transition at 14 MHz, also shown in Fig. 6, is complete at 60 K. The surface resistivity at 3 GHz and 4 K increases from 2 m Ω for an ac field of 10^{-4} Oe to 7 m Ω at 10^{-1} Oe. There still are weak links in the surface, but the material is competitive with the best bulk 123 seen to date. Similarly, light output during thermally stimulated luminescence (TSL) is quite low, implying the relative absence of insulating surface impurities.

TGA shows an oxygen uptake of 0.065 % above 300 C, part of which is metastable. The permanent mass gain is 0.04 %. This suggests that there has been some de-oxygenation during the hot pressing, but we have not yet obtained XRD to establish the amount and identity of the de-oxygenated component. The TGA pattern after re-oxygenation suggests essentially pure 124.

A comparison of the 10 K magnetization and hysteresis measurements on the hot pressed, oriented flakes with those of the parent powder (430B) indicates a reduction in both the average magnetization and in its hysteretic width to about 60 %.

6. Conclusions

Our work to date can be divided into powder production, materials characterization, and bulk manufacture. We feel that the powder production process is well in hand and that we can access and utilize a number of inter-disciplinary materials characterization and evaluation techniques to control and improve the quality of our product.

The manufacturing, forming and deforming of bulk shapes at elevated temperatures has just been started. Here the main challenge will be to maintain the correct oxygen pressure, so as to avoid decomposition and de-oxygenation, while allowing the grains to grow and deform.

Fig. 6. Transition Curves for Hot Pressed Flakes. The onset portion is also displayed enlarged by 10X. Note differences between dc and rf measurements, but nearly identical onset temperatures.

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