Polymer precursor synthesis and characterization of $YBa_2Cu_3O_{7-x}$

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We report the synthesis of $YBa_2Cu_3O_{7-x}$ prepared by a polymer precursor route. Polycrystalline single-phase materials have been produced in a porous morphology. The technique is also used to create fibers with diameters as small as several μm. The resistivity transitions are shown to be sharp with transition widths narrower than 1 K. Conductance fluctuations are measured in the vicinity of the superconducting transition and are consistent with three-dimensional superconductivity in the polycrystalline materials.

Advances in the field of superconductivity have recently been both rapid and dramatic. The discovery of a new class of ceramic oxide superconductors by Bednorz and Müller[1] and the observation that such materials exhibit superconducting transition temperatures above the boiling point of liquid nitrogen by Chu and his co-workers[2] has kindled a revolution of research activity in this area. Current research is directed both at the elucidation of the fundamental physics of the new superconducting phases and at the development of new and useful fabrication processes. To date most fabrication has been carried out using well-known procedures from ceramic technology in which thermodynamics controls the solid-state reactions. A multiplicity of substances can be formed in accordance with the appropriate phase diagram. For instance, early synthesis of $YBa_2Cu_3O_{7-x}$ produced both the green tetragonal insulating as well as the black orthorhombic superconducting materials and four phases were formed in the Bi, Ca, Sr, and Cu oxide system. Furthermore, the grains have a range of size and vary in their intergrain contacts as governed by a Boltzmann distribution of surface free energies.

Fabrication of thin films by evaporation, laser, and molecular-beam techniques[3,4] produced excellent superconducting materials with very high critical current density. Organic compounds have been used in coprecipitating metal carbonate from nitrate solutions,[5] and spin coating of metal carboxylates.[6] Also, synthetic polymers have been used to thicken solutions of metal compounds to facilitate spinning.[7] The metal compounds separated upon removal of the solvent in these processes.

Here we report[8,9] on a novel precursor technique to produce high-T_c superconductors based on homogeneous metal-polymer complexes. This new technique has been used to produce free-standing thin films and micrometer-diameter fibers, with both uniformity and control of grain size and grain contacts. Advantages of the technique include a ten times shorter calcination and annealing time and the direct formation of single-phase material. The synthesis of $YBa_2Cu_3O_{7-x}$ and its characterization are described below. The technique is generally useful; we have also separately and directly synthesized Y_2BaCuO_5,

various compounds in which Ni has been substituted for Cu and three of the reported phases of the Bi, Ca, Sr, and Cu oxide system.

Traditional ceramic techniques involve grinding metal compounds in the proper ratio to bring them into proximity. The metal ions in the respective crystalline compounds diffuse into the others via interfaces in contact or through external diffusion. Repeated regrinding and calcination under carefully controlled conditions can lead to a single desired phase as has been successfully demonstrated by a variety of research groups.

In our new technique, a polymer-metal complex precursor is first prepared in which the various metal ions in desired stoichiometric ratio are homogeneously and uniformly complexed to the polymer. This polymer-metal complex precursor is either cast into a clear film or spun into transparent fibrils. In the A-stage reaction under nitrogen, the organic polymer is pyrolyzed while the metal compounds react to form intermediate intermetallic compounds which are converted in the second B-stage reaction in the presence of oxygen to form the desired high-T_c superconductors. The success of the A-stage reaction depends upon the choice of a polymer which has comparable complexation affinities for all the metal compounds involved. The uniformly distributed metal ions react with the other ions in close proximity; the process is kinetically controlled. Another basis for the choice of the polymer is that it have low enthalpy of polymerization; such a polymer depolymerizes upon heating above the ceiling temperature (the polymer "unzips" into volatile monomer units).

For the specific case of $YBa_2Cu_3O_{7-x}$, methacrylic acid (68.8 g, 0.8 mol, Aldrich) was dissolved in 100 g of dimethyl formamide, and 2 g of tertiary butylhydroperoxide was added as initiator. Polymerization was carried out under a nitrogen atmosphere at 110 °C for 1 h to complete conversion. The molecular weight of the resulting poly-(methacrylic acid) was 500 000 according to gel permeation chromatography. The polymer-metal complex precursor was prepared by dissolving 34.4 g of poly-(methacrylic acid), 1.825 g of $Y(NO_3)_3 \cdot 5H_2O$ (0.005 mol), 2.614 g of $Ba(NO_3)_2$ (0.01 mol), and $Cu(NO_3)_2 \cdot 3H_2O$ (0.015 mol) in 50 ml of dimethyl formamide and

200 ml of H_2O. A clear brown-colored solution was formed.

The precursor solution was cast onto a glass plate and heated gradually from room temperature to 200 °C and kept at 200 °C for 1 h to evaporate the solvents. Transparent light-brown-colored film was obtained. Microscopic examination showed no crystallization of any metal nitrates. In an alternate technique, the precursor solution was extruded with a syringe. The extrudate was heated with a hot air gun, and the dry fiber was taken up on a mandrel. The transparent fibrils were also free of metal nitrate particles according to microscopy.

In the A-stage reaction, the precursor film or fiber was heated in an aluminum boat at 400 °C for 1 h under nitrogen. The product was subsequently heated (B-stage reaction) at 910 °C for 1 h under flowing oxygen and cooled to room temperature in 20 min. The resulting high-T_c superconducting material had the characteristics as described below. We note that the traditional ceramic technique preparation of $YBa_2Cu_3O_{7-x}$ as practiced in our laboratory requires 12 h heating under oxygen and 5 h of gradual cooling to room temperature; the new technique described here is much more rapid. During the A-stage reaction, the oxygen in the nitrate ion combines with the metal ions to form some intermediate intermetallic oxides even under the N_2 atmosphere while the polymer was depolymerized into methacrylic acid. In the B stage, the intermediate species of low oxygen content was transformed to the superconducting phase with the correct amount of oxygen deficiency.

There are several variables which affect the morphology and microstructure of the product. The molecular weight of the polymer and its concentration determines the viscosity of the precursor solution. These can be adjusted to produce fibers having diameters from 1 to 100 μm. The grain size and grain contact are dependent on the polymer-metal ratio and on the temperature duration of the B-stage reaction. Relatively uniform size grains from 0.1 to 50 μm can be obtained. Such specimens with various grains sizes are being studied to further understand the influence of grain size and contact on Josephson tunneling between grains.

The microstructures of samples of $YBa_2Cu_3O_{7-x}$ film and fiber are shown in Figs. 1(a) and 1(b), respectively. The former had a porous "foamlike" morphology with many crystallites of approximately the same size having extensive grain intergrowth. This is attributed to the kinetic control of our fabrication process. If the material of Fig. 1(a) is annealed at 950 °C for 12 h under oxygen, thermodynamically controlled recrystallization occurs to produce well-formed crystallites having the longest dimensions in the range 1–60 μm. Following the annealing, there are greatly reduced numbers of intergrain contacts of a tenuous nature.

The planes of the grains lie preferentially in the plane of the specimen because they are obtained from a precursor film. X-ray diffraction of the material contains all the reflections reported for the single-phase $YBa_2Cu_3O_{7-x}$. There were no extraneous reflections. Because of this preferential orientation, all the 00l reflections have much higher relative intensities than the other hkl reflections.
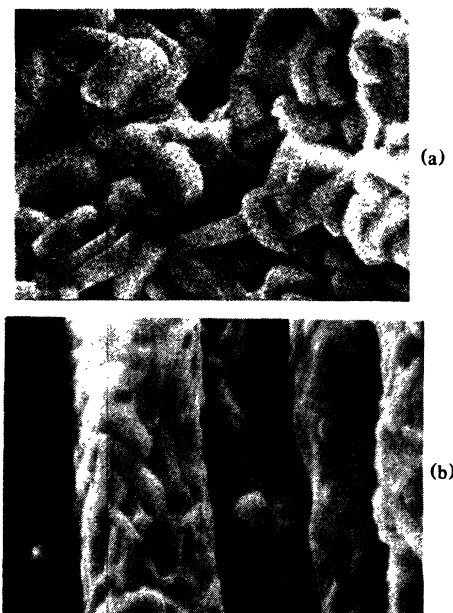

FIG. 1. SEM images of polycrystalline $YBa_2Cu_3O_{7-x}$ as prepared by the polymer precursor technique described in the text. (a) A high magnification image of a portion of foamlike low-density bulk material. (b) Filament of approximate diameter 10 μm.

An electron micrograph of free-standing $YBa_2Cu_3O_{7-x}$ fibril prepared by our technique is shown in Fig. 1(b). The fibril is comprised of crystallites tightly packed along the fiber axis in a partially oriented manner. For the smallest crystallite sizes (< 1 μm) the resulting fibers are relatively flexible (a 10 cm length of 10 μm diameter fiber can be readily bent to a 120° angle without breaking).

Elementary resistivity measurements were carried out as a function of temperature. The various samples were located in an helium atmosphere in a sealed chamber. Four-terminal electrical contact was made with silver-loaded conducting paint. The temperature inside the chamber was measured with calibrated diodes. Data were collected during gradual warming or cooling runs. There was no hysteresis; for a given sample, data collected on warming were indistinguishable from that taken on cooling. Examples of resistivity transitions[9] observed in dc electrical resistance measurement for typical foamlike and fiber morphologies are shown in Fig. 2. Figure 2(a) is an illustration of the temperature-dependent resistivity for a foam material which shows that the transition region (10%–90%) is quite narrow. These transitions appear as sharp as any reported in the literature. The resistivity falls nearly linearly from room temperature. Figure 2(b) is an example taken from dc measurements on a bundle of fibers each of approximately 5 μm diameter. Noticeable in this figure is a resistive "foot" on the low-temperature side of the transition. This "foot" is non-Ohmic in the sense that its relative size and shape changes with changes in the measuring current. A similar "foot" has been seen in measurements taken on bulk materials prepared by the more traditional ceramic techniques.[10] It is important to note that the above measurements were made on as-
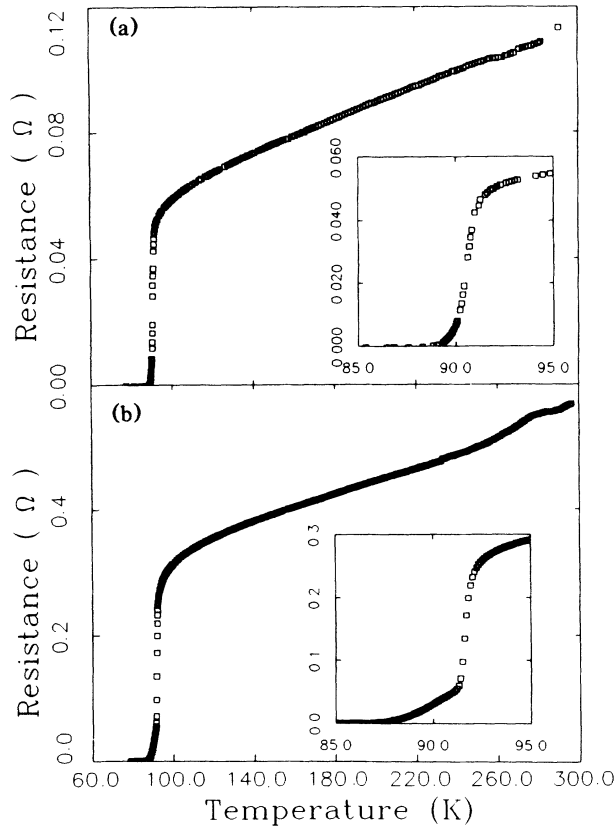
FIG 2. dc resistivity measurements of $YBa_2Cu_3O_{7-x}$ as a function of temperature (a) for a foamlike bulk sample and (b) for a bundle of filaments each of approximate diameter 5 μm.

synthesized materials which were not pulverized and recalcined as is the usual practice. Therefore, the intergrain contacts may be different from those found in materials made conventionally.

Based on the measured cross-sectional area of the fiber bundle used for the measurement shown in Fig. 2(b) and the observed critical current at 4.2 K, we place a lower limit on the critical current density of 1000 A/cm^2 at 4.2 K. This is conservative since a microscopic examination of the individual fibers reveals that there are voids apparently of random size and location distributed along the axis of the fiber. Thus, we are unable to obtain a definitive measure of the minimum macroscopic cross-sectional area. A future goal of our efforts will be to minimize the presence of the voids through variations in the synthesis.

We have also carried out ac susceptibility measurements on various materials produced by this technique. An example of such a measurement is shown in Fig. 3. Here a mutual inductance technique[11] was used at 10 kHz on a foamlike sample. The same sample was subjected to a dc resistivity measurement and the resistive transition is also shown in the figure. As the temperature is lowered, the susceptibility transition begins in earnest only after the resistivity transition has nearly reached completion. This effect seems to be a common feature of these materials and has been seen in oxide superconductors produced by ceramic techniques.

Although the materials we have fabricated are not spatially uniform (due to voids), we have carried out an analysis of the excess conductivity in the vicinity of the superconducting transition and compared the results with expectations based on superconducting fluctuations. Both the polycrystalline foamlike materials and the fibers demonstrate behavior close to that expected for three-dimensional superconductivity. This behavior has also been observed for polycrystalline materials prepared by the more customary ceramic techniques.[12] We illustrate this behavior for these materials in Fig. 4. To obtain these plots, we have extrapolated the resistivity measured for the temperature range 180 $< T <$ 240 K to the vicinity of the resistivity transition and computed the conductivity in excess of the extrapolation, $\Delta\sigma$. A plot of $(\Delta\sigma)^{-2}$ versus temperature is linear within several degrees Kelvin of the transition and the $(\Delta\sigma)^{-2} = 0$ intercept yields the transition temperature T_c. For both of the cases illustrated, the transition temperature determined in this manner was observed to be the midpoint of the resistive transition. For a three-dimensional superconductor the excess conductivity is given by[13,14]

$$\Delta\sigma = \frac{2\pi e^2}{32h\xi_{GL}t},$$

where e is the electron charge, $\xi_{GL} \sim t^{-1/2}$ is the Ginzburg-Landau coherence length, and t is the reduced temperature, $t = (T - T_c)/T_c$. The logarithmic plots in Figs. 4(a) and 4(b) have slopes near $-\frac{1}{2}$ as expected for three-dimensional superconductivity. Given the polycrystalline nature of the samples, this is perhaps not surprising. σ_0 is the room-temperature value of the resistivity.[15] The two-dimensional expression[14] for the enhanced conductivity did not fit the data.

For a superconductor in the dirty limit $(l \ll \xi_0)$, $\xi_{GL} = 0.85(\xi_0 l)^{1/2} t^{-1/2}$; for the clean limit $(l \gg \xi_0)$, $\xi_{GL} = 0.74\xi_0 t^{-1/2}$. Here, ξ_0 is the BCS coherence length and l is the mean free path. The $\ln(t) = 0$ intercept of the straight line fits to the data of Fig. 4(a) allows an estimate of quantity $(\xi_0 l)^{1/2}$ or ξ_0 subject to the uncertainty of the
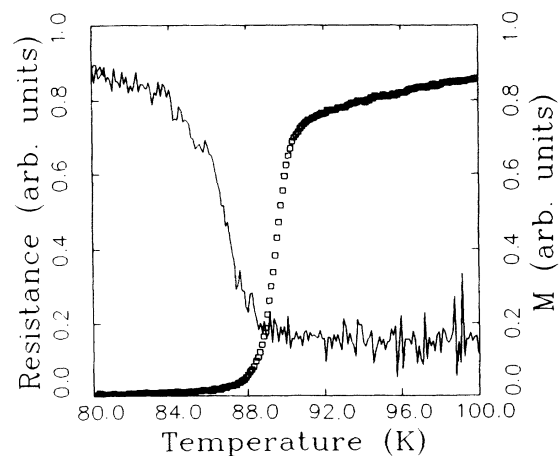

FIG. 3. Example of a dc resistivity measurement (open squares) and an ac susceptibility measurement made on a foamlike low-density sample of $YBa_2Cu_3O_{7-x}$ prepared by the polymer precursor technique. The susceptibility measurement was made by a mutual inductance (M) technique.
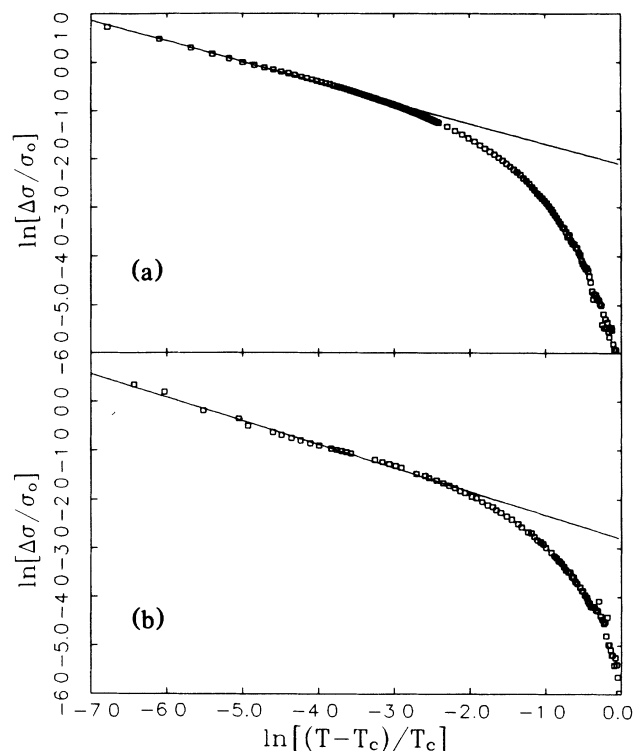
FIG. 4. $\ln(\Delta\sigma/\sigma_0)$ vs $\ln[(T-T_c)/T_c]$ for samples with (a) filamentary and (b) bulk foamlike morphology.

cross-sectional area discussed earlier. Under the assumption that our material is in the clean limit, we find $\xi_0 \simeq 1.8$ nm for the fiber sample; the cross-sectional area of the foamlike sample was even more difficult to estimate precluding an estimate of ξ_0 for that sample. If we are in the dirty limit, then our results are consistent with

$(\xi_0 l)^{1/2} \simeq 1.5$ nm.

Recently the appropriateness of fluctuations in the case of the ceramic oxide superconductors in any context has been called into question by Bhattacharya et al.[16] on the basis of ultrasonic measurements. We have examined temperature derivatives of our resistivity data over the region $T_c < T < 200$ K and find no clear evidence for a change of behavior at a characteristic temperature; rather, the change in the magnitude of dR/dT appears to evolve continuously from temperatures above 150 K. In addition, the excess conductivity, as seen in Figs. 4(a) and 4(b), clearly appears to diverge as a power law in the reduced temperature. On the basis of our resistivity measurements, we believe the three-dimensional fluctuation model adequately describes the data for these materials and we see no evidence for a "transition" at higher temperatures.[16]

In conclusion, we have developed a novel polymer-metal complex precursor technique for the fabrication of high transition temperature superconductors. The principles involved in the reactions of this process are different from other known methods. Definite advantages and differences between this and other techniques have been pointed out and demonstrated. The new technique is a simple, rapid, and direct process which may provide a method of industrial production of fibers and filaments of high-T_c superconductors.

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[15]The room-temperature resistivity for the fiber bundle sample studied was $\sigma_0 \simeq 500$ $(\Omega \, cm)^{-1}$.

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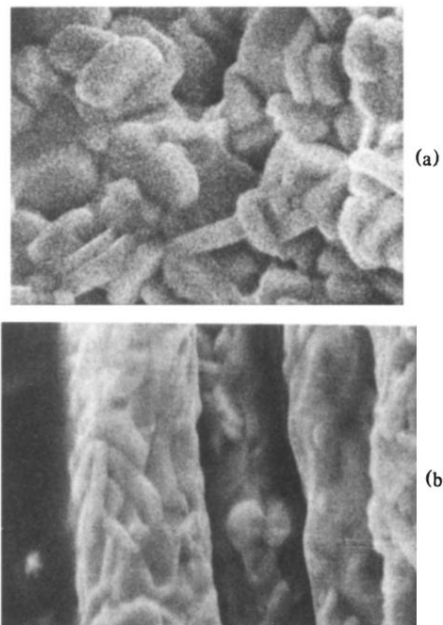
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