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January 1988

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Versatile new metalorganic process for preparing superconducting thin films

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(Received 27 October 1987; accepted for publication 20 November 1987)

A new technique for producing thin films of the high-temperature perovskite superconductors, $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$, where Ln represents a rare-earth element, using spin-on metalorganic precursors is described. Pyrolysis of the spin-coated films, consisting of mixed metal (2-ethyl hexanoates), leads to black films up to several microns thick whose degree of orientation is a function of the processing temperature and duration. Representative films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ on MgO begin to exhibit orientation with the *c* axis perpendicular to the film plane at heat treatments above 900 °C. The superconducting behavior of a highly oriented film produced at 990 °C is characterized by T_c (onset) = 89 K, T_c ($R = 0$) = 77 K, and $J_c = 10^3 \text{ A cm}^{-2}$ at 65 K.

The recent discovery of materials that exhibit superconductivity at 90 K¹ has generated much interest in developing their technological applications. These cuprate superconductors, of composition $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$,² where Ln is a rare-earth element, have now been prepared by a variety of physical and inorganic chemical techniques. The standard route to preparation of bulk materials involves mixing the elements as the oxides, carbonates, nitrates, oxalates, etc. followed by sintering at elevated temperatures.³ Thorough mixing of the components to produce a homogeneous mixture remains a problem with the solid-state route. Thus, repeated milling and sintering cycles are needed to achieve the proper phase. Thin films, on the other hand, have required more sophisticated techniques. Superconducting thin films have been produced by *e*-beam evaporation,⁴ sputtering,⁵ molecular beam epitaxy,⁶ and laser desorption.⁷

Our interest lies in developing new methods for bulk and thin-film preparation using homogeneous solution techniques. Mixing at the molecular level should improve formation of the desired material and crystallographic phase. The strategy we are pursuing involves synthesis of metalorganic precursors for the elements of interest. Solutions of the combined precursors are spin coated and fired to produce superconducting films from a few thousand angstroms to several microns thick. Alternatively the homogeneous solution can be evaporated and the resulting solid pyrolyzed to give powders of the superconductor.

Copper bis(2-ethyl hexanoate) [$\text{Cu}(\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2)_2$], barium bis(2-ethyl hexanoate) [$\text{Ba}(\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2)_2$], and yttrium tris(2-ethyl hexanoate) [$\text{Y}(\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)(\text{CO}_2)_3$] were prepared by published methods.⁸ As it is common for metal carboxylates to retain solvent of crystallization in their coordination sphere, the metal content of the precursors was determined by thermogravimetry (TG) in O_2 using a Perkin-Elmer thermal analysis system 7. The carboxylate precursors were dissolved in chloroform in the ratio 1 Y:2 Ba:3 Cu to give homogeneous solutions, whose viscosity was adjusted by varying the concentration. A typical sample prepared using the mixed carboxylates solution (1 M [Cu]) at a spin speed of 2000 rpm gave a final film thickness of $\sim 1.4 \mu\text{m}$. Films were pyrolyzed in a programmable tube furnace under a steady flow of O_2 . Film thicknesses were calculated on the

basis of weight gain using a density for the superconductor of 6.3 g cm^{-3} .

The selection of precursors for the metalorganic route to superconductors was based on the following desired properties: (1) complexes of the different elements should be mutually compatible; (2) precursors should be soluble in a solvent suitable for spin coating; (3) precursor solutions should form homogeneous, continuous films; (4) precursors should decompose cleanly, i.e., leave no residual carbon. Our previous experience with palladium acetate⁹ led us to look at carboxylate complexes of Cu, Ba, and the rare earths. In these complexes, the two O atoms of each carboxylate are bonded directly to the metal and the organic substituent has a direct effect on the solubility. A long hydrocarbon chain improves the solubility of the complex in organic solvents. The carboxylate that we chose for our initial studies, 2-ethyl hexanoate (abbreviated 2-EH), is shown in Fig. 1. The Cu^{2+} , Ba^{2+} , and Ln^{3+} complexes contain, respectively, 2, 2, and 3 molecules of 2-EH. TG of these complexes in O_2 shows that complete decomposition to the respective oxides, CuO, BaO, and Y_2O_3 , occurs at 300, 379, and 322 °C. Chloroform solutions of the complexes are prepared in the molar ratio 1 Y:2 Ba:3 Cu. The use of these homogeneous solutions favors uniform formation of the superconducting material.

A typical sample is prepared by spin coating a substrate such as ZrO_2 or MgO at 2000 rpm or dipping the substrate in the solution and drying horizontally. MgO and ZrO_2 substrates were used in these preliminary studies to prevent harmful interaction with the ternary ceramic material. Prebaking at 100 °C removes the residual solvent. Samples are then fired in a steady stream of O_2 to a maximum temperature of 800–990 °C followed by annealing at 400 °C. The TG results suggest that complete pyrolysis of the films and removal of organic components occur by 400 °C. Continuation of the processing to higher temperatures achieves solid-state reaction of the materials and increasing grain growth. The x-ray diffraction patterns of films fired at different maximum

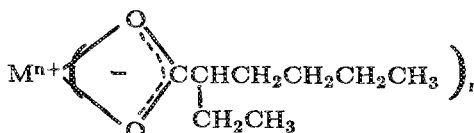


FIG. 1. Representative structure of a metal 2-ethyl hexanoate complex.

temperatures and annealed at 400 °C are shown in Fig. 2. Notice the increasing degree of *c*-axis orientation perpendicular to the film plane with increasing process temperatures. The high-temperature step in the processing is extremely short, 3 min at the maximum. Despite the high temperature needed to achieve orientation, the short processing times may preclude significant interaction of the film with the substrate. Scanning electron micrographs of these same films are shown in Fig. 3. The sample prepared at 990 °C contains platelets of material (Fig. 4) that must be related to the high degree of *c*-axis orientation seen in the x-ray diffraction pattern [Fig. 2(a)]. At lower temperatures we find the smaller grain size associated with more random crystallographic orientations.

The superconducting characteristics of these films are extremely promising for further development and applications. Figure 5 shows a plot of resistivity versus temperature for the film processed at 990 °C. Note the metallic behavior of the film above the superconducting transition temperature. The onset of the superconducting transition occurs at 89 K, $T_c(R=0) = 77$ K, and J_c , measured at 65 K, is about 10^3 A cm⁻². We are in the process of analyzing our films to determine the level of contamination that might be present. Our TG results lead us to believe that C contamination in these films should be minimal.

During the preparation of this manuscript we became aware of related work using metal acetates¹⁰ and naphthenates.¹¹ The former method suffers from the limited solubilities of the metal acetates, such that hot aqueous acetic acid solutions of the acetates must be used in order to spin coat a homogeneous film. This solubility problem often leads to precipitation of the metal complexes during the rapid cooling of the spin-coating process, producing an inhomogeneous film. It also places severe limits on the achievable film thickness. The 2-EH precursors that we use are more soluble

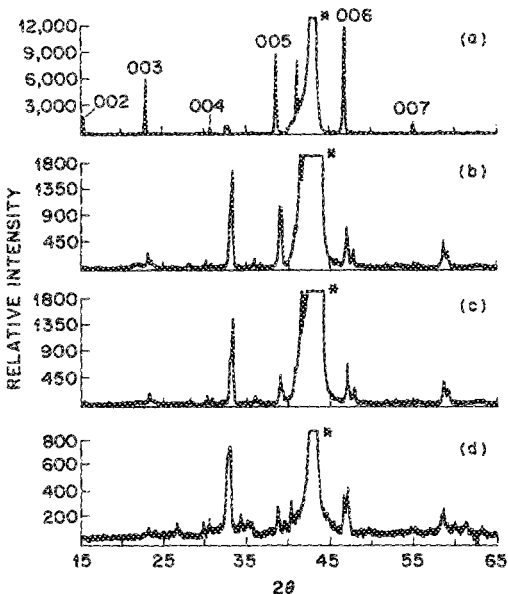


FIG. 2. X-ray diffraction pattern of a $\sim 1.4\text{-}\mu\text{m}$ $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film formed by pyrolysis at (a) 990 °C, (b) 950 °C, (c) 900 °C, and (d) 825 °C. Diffraction lines of the MgO substrate are indicated by *.

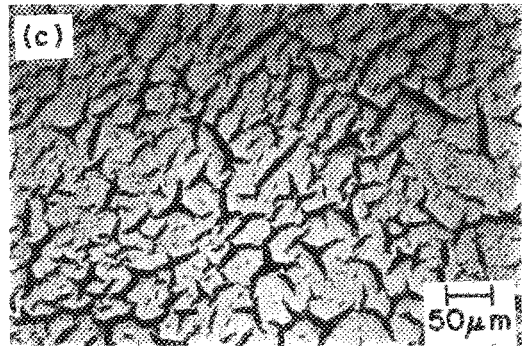
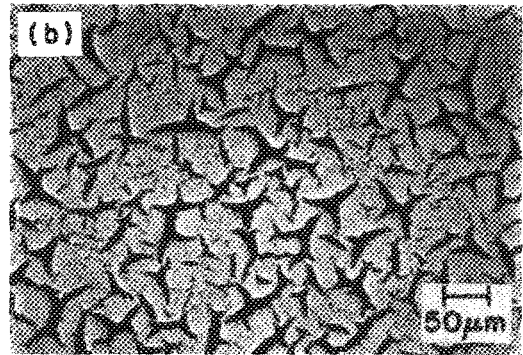
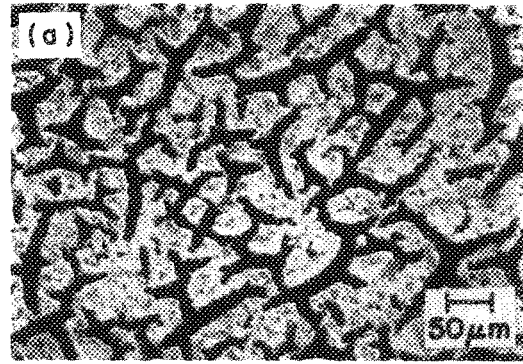


FIG. 3. Scanning electron micrograph of a $\sim 1.4\text{-}\mu\text{m}$ $\text{YBaCu}_3\text{O}_{7-x}$ film formed by pyrolysis at (a) 990 °C, (b) 950 °C, and (c) 900 °C. White areas correspond to the superconducting material. Dark areas are the MgO substrate.

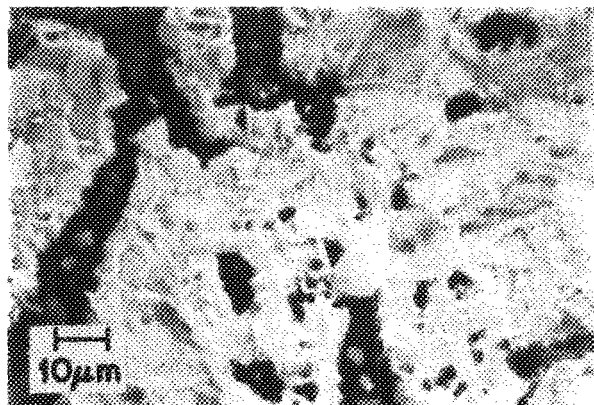


FIG. 4. Scanning electron micrograph at higher magnification of a 990 °C film shown in Fig. 3(a).

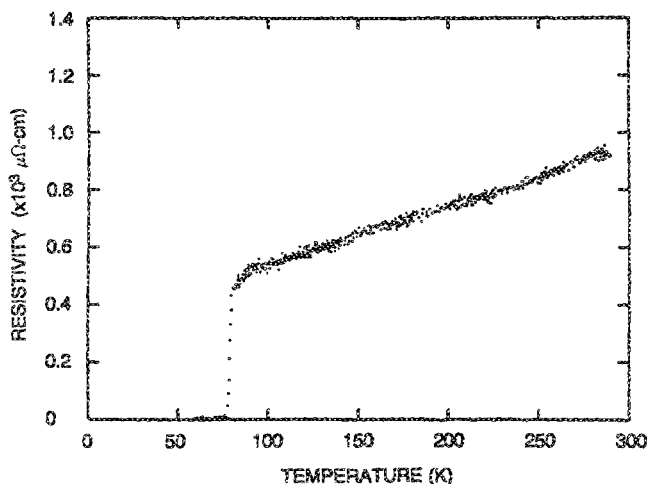


FIG. 5. Resistivity vs temperature for a $\sim 1.4\text{-}\mu\text{m}$ $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film.

than the acetates, allowing us a much greater flexibility in choice of film thickness. The electrical characteristics of our films are also superior to those reported for the acetate process. We have produced films of $\text{ErBa}_2\text{Cu}_3\text{O}_{7-x}$ from spin-coated acetate solutions to compare processes. These Er films exhibit much improved electrical characteristics [T_c (onset) = 80 K; T_c ($R = 0$) = 66 K] over the reported Y acetate work, but we are not optimistic about the utility of this process in light of our success with the 2-EH complexes. Results of the Er work will be discussed elsewhere.¹²

The reported metal naphthenate process involves formation of 1–3 μm thick films by ten successive dip/pyrolysis cycles.¹¹ Our experience shows that applying films of varying thicknesses by a single spin coating or several spin coats as needed produces significantly greater film uniformity and continuity compared with the dip process, although the latter is equally usable with our materials. The reported films have a T_c (onset) = 90 K yet reach $R = 0$ at 60 K with a tail that suggests impurities or inhomogeneities.

Another interesting film preparation technique employs sol-gel precursors.¹³ The electrical characteristics of these films are extremely good; however, the sol-gel process requires slow heating with times on the order of 48 h to drive off solvent.

We have demonstrated a versatile new technique for preparation of high-temperature cuprate superconductors. Metalorganic solutions are used to deposit films by spin coating, dipping, brushing, or spraying. The electrical char-

acteristics of our films are better than those reported for other solution application techniques and the spin coating one process offers the greatest versatility. Extremely short processing times of three minutes at 990 °C give highly oriented superconducting films with the c axis perpendicular to the film plane. Processing at lower temperatures for similar times produces more randomly oriented films. This preliminary report represents the beginning of more extensive studies into the variety of applications of our metalorganic process. Many experiments are in progress to decrease the width of the superconducting transition, the morphology of the films, and the applications of the metalorganic precursors.

Note added in proof. We have found that films of less than 1 μm do not exhibit the cracking seen in the thicker films. Films prepared by two successive coatings of 0.5 μm formed by pyrolysis at 990 °C show improved $J_c = 10^4$ A cm^{-2} at 65 K with T_c similar to the above films.

We are indebted to H. M. O'Bryan for helpful discussions.

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