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# Polymer precursor synthesis of high $T_c$ superconductors

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## Summary

Free standing oxygen deficient perovskite $Y_1Ba_2Cu_3O_x$ has been synthesized from polymer precursors. As prepared the material is comprised of crystallites of uniform and extensively interconnected morphology. The decrease of resistivity with temperature is perfectly linear, the onset of $T_c$ occurs at 92.4 K and $T_c$ (90%-10%) is ca. 1K. This precursor method of synthesis requires much lower temperature and shorter time than the usual ceramic techniques. Both free standing films and fibers can be obtained which is not possible otherwise.

## Introduction

The discovery of high $T_c$ (35K) superconductivity in a layered perovskite oxide composed of La, Ba, and Cu is of such importance that Bednorz and Muller (1) were awarded a Nobel Prize within the year. Now, materials have been found with $T_c$ above 90K (2-4) of Y, Ba, and Cu. These substances are up to now prepared by the ceramic technology. A typical procedure (4) involves, mixing $Y_2O_3$, $BaCO_3$ ,and CuO, grinding, and heating at 950°C in air for 1 day, pressed into pellets, sintered in flowing $O_2$ for 16 hrs, cooled to 200°C in $O_2$, then overnight treatment in $O_2$ at 700°C. Such method affords little if any control on the size or shape of the crystallites or intergrowth between them.

We have discovered a new polymer-metal-complex (PMC) precursor (5,6) synthesis of high-$T_c$ superconductors which offers several important advantages over the ceramic methods: (1) formation of the desired single phase, (2) uniform grains of controled sizes, (3) lower temperature < 910°C instead of > 950°C, (4) shorter fabrication time one hr. instead of days, (5) free standing films and fibers. The $Y_1Ba_2Cu_3O_x$ synthesized by th PMC precursor method exhibits as good superconducting properties as those obtained by optimized ceramic techniques.

## Experimental

Methyl methacrylate was polymerized to a molecular weight of ca. $10^6$,the polymer was hydrolyzed to ca. 90% completion to form a random poly(10 methyl methacrylate-co-90 methacrylic acid). The copolymer was dissolved in dimethyl formamide and yttrium, barium and copper nitrates or iodides in 1:2:3 mole ratios were added to form a clear PMC solution. The total number of moles of metal compounds correspond to 60 mole percent of the methacrylic acid content in the copolymer. The solution was casted into a transparent polymer precursor film by solvent evaporation at 200°C. The film was prepyrolyzed at 500°C in an alumina boat under flowing nitrogen for 2 hrs, heated at 910$^{o}$C under flowing $O_2$ for 1 hr. and cooled rapidly to 200$^{o}$C in 20 min. to give a low density film of high-$T_c$ superconductor. To produce filaments of $Y_1Ba_2Cu_3O_x$. The PMC 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. This PMC precursor fibers were converted to high-$T_c$ filaments as before.

## Results and Discussion

The free-standing fiber of $Y_1Ba_2Cu_3O_x$ obtained with the PMC-precursor method is comprised of grains of uniform size. Depending upon the fabrication conditions the grain sizes ranged from 0.1 to 50 microns, Figure 1 is an SEM micrograph of a specimen with average grain size of 5x3x1.5 microns. All the particles are intergrown into one another. In contrast, the same compound obtained with ceramic


Figure 1. SEM micrograph of as prepared $Y_1Ba_2Cu_3O_x$, 4400x magnification.

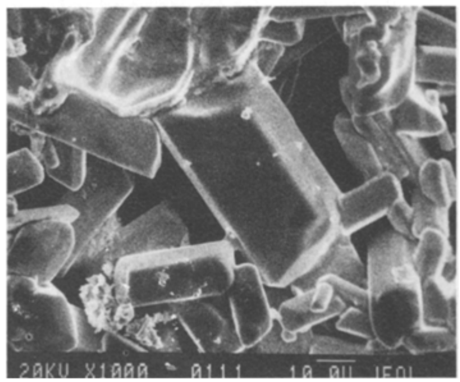

Figure 2. SEM micrograph of sample in Figure 1 after sintering, 1000x magnification

technology is characterized by very broad particle size distribution and very little intergrowth. This is best demonstrated by pulverizing the material of Figure 1, pelletized at 30,000 psig and sintered at 950$^{o}$C for 12 hrs. Figure 2 showed evidence for recrystallization process forming crystallites having dimensions from several to 50 microns. There is now very few and tenuous intergrowth between grains (Figure 3). A SEM micrograph of free-standing $Y_1Ba_2Cu_3O_x$ fibril prepared by our PMC-precursor technique is shown in Figure 4. Th fibril is comprised of crystallites tightly packed along the fiber axis in a partially oriented manner.

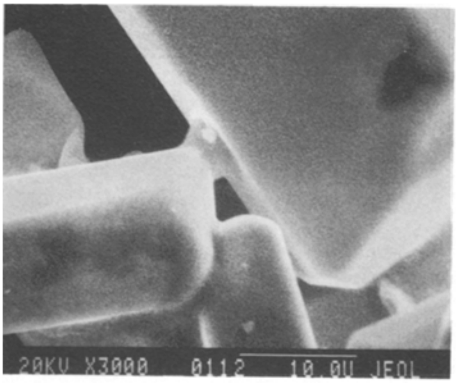


Figure 3. SEM micrograph of sintered $Y_1Ba_2Cu_3O_x$, 3000x magnification.

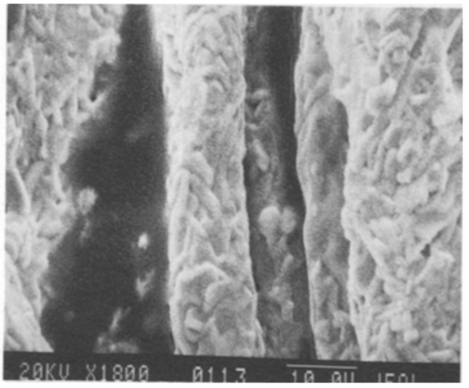


Figure 4. Filament of $Y_1Ba_2Cu_3O_x$, approximately 10 micron in diameter.

Samples prepared by ceramic process required long sintering and additional high temperature treament to improve superconducting properties (4). The latter is usually necessary to develop intergrain growth. In contrast, the materials as prepared by the PMC-precursor method displays a very linear decrease of resistance with temperature (Figure 5). The superconducting transition is as sharp as any reported in the literature; the $T_c$ for 90% to 10% of resistivity is less than 1K. The onset of $T_c$ begins st 92.4K; the midpoint of the trasition is 91.2K.

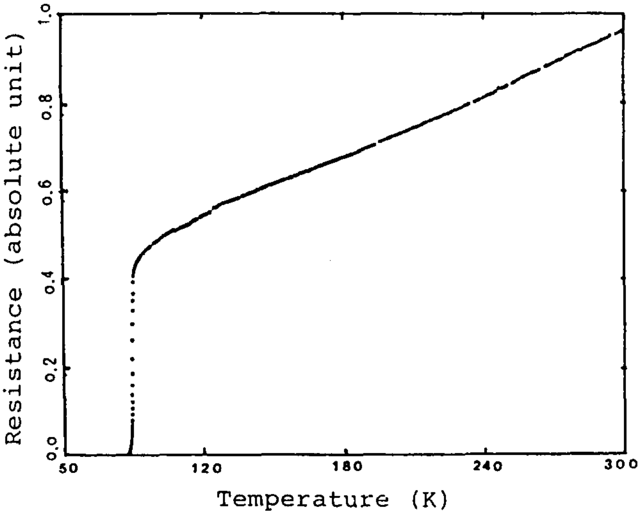


Figure 5 Resistance versus temperature plot for samples of Figure 1.

The free-standing filament of $Y_1Ba_2Cu_3O_4$ prepared by the PMC-precursor process has critical current density in excess of $10^3$ $Acm^{-2}$ (6). Detailed analysis of the resistivity versus temperature data is consistent with a three dimensional superconducting fluctuation model(6).

The important variables in the PMC-precursor synthesis are the choice of the metal compounds, the polymer, their ratios, the solvent, pyrolysis conditions, calcination temperature and time, and quenching rate. Their effects on the yield, grain size, and morphology of the high-$T_c$ superconductor will be published elsewhere (7). This new synthesis technique has been applied to several other known high-$T_c$ superconductors as well as semiconductors of interest to the field.

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