

## Preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor by coprecipitation of nanosize oxalate precursor powder in microemulsions

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Received 7 December 1992

We describe a new technique for the synthesis of ultra-homogeneous nanoparticles of precursor oxalate powders by coprecipitation in the aqueous cores of water-in-oil microemulsions for the preparation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (1-2-3) oxide superconductors. This novel technique ensures uniform mixing of cations down to the scale of 10 nm. This ultrafine powder results in phase pure "1-2-3" oxide superconducting material of almost theoretical density and > 93% Meissner shielding expected from an ideal sample ( $-1/4\pi$ ) after proper heat treatment.

### 1. Introduction

Since the discovery of superconducting transition temperature near 30 K in La-Ba-Cu oxide by Bednorz and Müller [1], enormous efforts were made to study perovskite-like oxide superconductors. This led to the invention of new superconducting materials in Y-Ba-Cu-O [2,3] systems with  $T_c$  higher than the boiling point of liquid nitrogen. Recently, even higher  $T_c$  phases were discovered in Bi-Sr-Ca-Cu-O [4] and Tl-Ba-Ca-Cu-O [5] systems.

The properties of oxide superconductors are strongly dependent on the synthesis techniques and the processing conditions. Therefore, the powder synthesis techniques are likely to play a crucial role in the preparation of bulk materials. The conventional method of preparation for the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  by means of solid-state reaction has many inherent problems, e.g. poor homogeneity, large particle size, lack of reproducibility and longer heat treatment times. This approach usually requires several heating and grinding cycles. In order to achieve an acceptable level of homogeneity, wet chemical techniques such as coprecipitation [6–15] and freeze drying [16] have also been used. Homogeneous coprecipitation has been widely employed by various workers for precursor powder synthesis with better homogeneity and stoichiometry and is widely used

for the manufacture of high-quality ceramics [17–22]. Homogeneous coprecipitation of carbonates by  $\text{K}_2\text{CO}_3$  in the presence of KOH [8] would lead to the contamination of precursor powder by potassium ion. Other efforts using oxalate ion as precipitant have been hindered by the resultant undesirable stoichiometry [9,10] due to differing solubilities of individual oxalates. The use of ammonium oxalate as precipitant directly, would lead to complexing of  $\text{Cu}^{2+}$  ions with ammonia molecule. Because of the differing solubility of metal oxalates, it is necessary to optimize the reaction environment carefully (i.e. pH and precipitating medium) to obtain the desired stoichiometric ratio in the precursor powder. The variation of stoichiometry with pH in aqueous medium has been reported [17,23,24]. Recent efforts focus on the use of non-aqueous solvents to reduce the solubility of oxalates [25–27]. We have recently reported almost complete (> 99.9%) precipitation of oxalates from acetic acid medium [28].

It is now well recognized that the properties of high-temperature superconductors are critically dependent on the microstructure of the sample. The control of size, size distribution, morphology of the precursor powder and the heat treatment conditions are critical for obtaining the desired microstructure. A wet chemical synthesis process results in a more homogeneous material compared to material obtained

by conventional solid-state reaction. Even better homogeneity can be achieved, compared to bulk coprecipitation, if the reaction can be carried out in a controlled environment nanosize reactor. The use of aqueous cores of water-in-oil microemulsions as nanoreactors for the chemical reaction offers this opportunity [29–32].

Microemulsions are thermodynamically stable isotropic dispersions consisting of nanosize domains of oil and/or water stabilized by an interfacial film of surface active agent. The precise control of the size and stability of the nanostructured domains provides a novel media for the preparation of mesoscopic particles of desired size and shape with a narrow size distribution. The precipitation inside the nanosize domains (usually 5–25 nm) of water in oil microemulsions would results in nanoparticles of uniform size distribution and better homogeneity compared to bulk coprecipitation which results in uncontrolled nucleation and growth. Microemulsions have been used to prepare inorganic catalysts with precisely controlled size and shape, 1–100 nm, including “quantum” particle and nanoparticles [33–35]. Recently we have reported the synthesis of nanosize precursor powders in the CTAB/butanol/octane/aqueous phase microemulsion system for the preparation of barium hexaferrite for high-density perpendicular recording [36].

The design and synthesis of materials with nanometer dimensions, so-called mesoscopic materials, are the subject of intense current research. Materials with particles in the size range 10–100 Å exhibit novel electronic, optical, magnetic and chemical properties due to their extremely small dimensions [37]. Fine grain, higher surface area materials are especially important in ceramic processing. Refractory materials can be processed to form more dense, and potentially fully dense, ceramics from ultrafine nanoparticles [38]. Although several studies have been devoted to the synthesis of nanometer-sized semiconducting and magnetic materials [39–46], relatively little work exists for the synthesis of high- $T_c$  oxide superconductors of similar dimensions. We have recently reported the synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  from ultrafine precursor powders coprecipitated, using ammonium oxalate as precipitant, in the aqueous core CTAB/butanol/octane aqueous core of water-in-oil microemulsion systems, of almost theoretical

density with 90% of ideal Meissner shielding at 4.8 K [47,48]. The use of ammonium oxalate as the precipitant requires precise control of pH to achieve correct stoichiometric ratio and results in incomplete precipitation. In this article we report the synthesis of nanosize precursor powders in nanosize domains of water-in-oil microemulsions consisting of acetic acid and water mixture. The use of acetic acid medium results in almost complete precipitation because oxalates of yttrium, barium and copper are insoluble in acetic acid.

## 2. Experimental

All the chemicals used, yttrium acetate,  $\text{Y}_2(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 4\text{H}_2\text{O}$ , barium carbonate,  $\text{BaCO}_3$ , and copper acetate,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , were of high purity (>99.9%). Acetic acid and cyclohexane were of reagent grade. Surfactant, Igepal CO-430, nonylphenoxy poly (ethylenoxy) ethanol,  $(\text{C}_2\text{H}_4\text{O})_4\text{C}_{15}\text{H}_{24}\text{O}$ , was of a commercial grade. Deionized distilled water was used in all the chemical procedures. Yttrium acetate, barium carbonate and copper acetate were first dissolved in 25/75 V/V acetic acid water mixture in a cationic ratio of 1:2:3. After evaporation to dryness, the residue was redissolved in 200 ml of 50/50 acetic/water mixture to 10 mM  $\text{Y}^{3+}$ , 20 mM  $\text{Ba}^{2+}$  and 30 mM  $\text{Cu}^{2+}$  concentration. A clear blue solution was obtained. Oxalic acid in 10% excess than that required stoichiometrically was dissolved in 50/50 V/V acetic acid/water mixture. For the preparation of particles, a microemulsion containing all the cations in the required stoichiometric ratio was mixed with another microemulsion containing oxalic acid in the aqueous phase. The nanosize domains (aqueous core of water-in-oil microemulsions) collide frequently and move about rapidly [29–32]. This allows the reacting species to come in contact when a microemulsion containing all the metal salts is mixed with another microemulsion containing the precipitating agent. Since both the microemulsions have the same surfactant, hydrocarbon and aqueous phase (differing only the nature of the salt dissolved), the microemulsion does not get destabilized on mixing. The steric barrier provided by the surfactant monolayer restricts the

growth of the precipitated oxalate particles and hinders intergrain coagulation. Serial precipitation of cations (which may occur in the conventional wet chemical methods) is avoided in the present approach, the upper limit of chemical inhomogeneity being set by the dimension of nanosize domains (usually 5–25 nm). The compositions of both the microemulsions used for the preparation of nanoprecursor oxalate particles are given in table I. The cations precipitate as Y–Ba–Cu oxalate particles by the reaction with oxalic acid within the nanosize domains of water-in-oil microemulsions. A schematic representation of the process and of the water-in-oil microemulsion is given in fig. 1.

The precipitate was separated in a superspeed centrifuge at 7000 rpm for 10 min. Then it was washed

Table I

Microemulsion I	Igepal CO-430 (15 g) + cyclohexane (50 ml) + aqueous solution of metal salts (10 ml) (Y:Ba:Cu = 1:2:3)
Microemulsion II	Igepal CO-430 (15 g) + cyclohexane (50 ml) + aqueous solution of oxalic acid (10 ml)

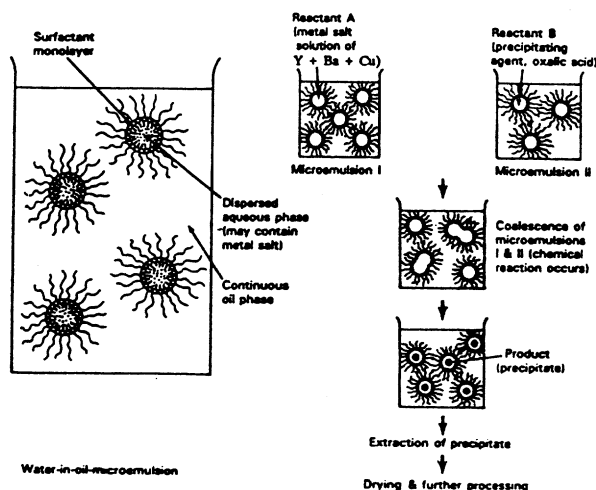


Fig. 1. Schematic of water-in-oil microemulsion and of the reaction mechanism.

repeatedly with 1:1 chloroform:acetone mixture to remove all the surfactant. A small drop of this suspension was placed on a TEM grid for particle size analysis. A JEOL-200 CX was used for the transmission electron microscopy studies. The precipitate was dried at 100°C in air for 12 h.

Thermogravimetric (TGA) and differential thermal analysis (DTA) studies were performed in air at a heating rate of 5°C/min by a Du Pont (TGA/DTA) 900 instrument. The dehydrated oxalate precursor powder was calcined at 800°C/min for 12 h in air and then slowly cooled (1°C/min) to room temperature. The calcined powder was pressed into a pellet of 6 mm diameter under a static pressure of 120 MPa, and then the pellet was sintered at 930°C for 12 h in flowing oxygen atmosphere. The chemical composition of the calcined powder was determined by energy dispersive X-ray analysis (EDAX). For inductively coupled plasma atomic emission spectroscopy (ICP/AES) analysis, calcined powder was dissolved in hot nitric acid. The structure and the phase composition were determined by a Philips powder X-ray diffractometer using Cu K $\alpha$  radiation at 40 kV, 20 mA. The instrument was calibrated with Si. The dc magnetic susceptibility measurements were performed using commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, CA). The surface morphology of the sintered specimen was examined by scanning electron microscopy.

### 3. Results and discussion

The nanosize domains of water-in-oil microemulsions act as batteries of constrained reactors for the precipitation reaction, as the surfactant monolayer provides a barrier restricting the growth of the oxalate particles. The steric barrier provided by the surfactant monolayer also hinders the coagulation of the particles. The transmission electron micrograph (fig. 2) of the precursor powder shows that the particles formed within the nanosize domains of the microemulsion are fairly monodispersed within the size range of 3–12 nm. However, few larger aggregates were also observed, which may be due to aggregation under high centrifugation force during the separation step.

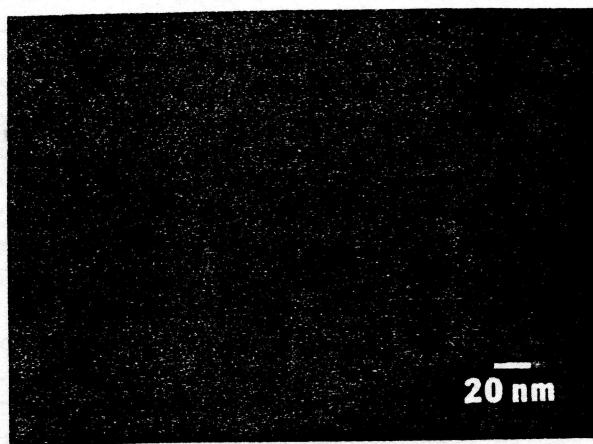


Fig. 2. Transmission electron micrograph of oxalate precursor powder.

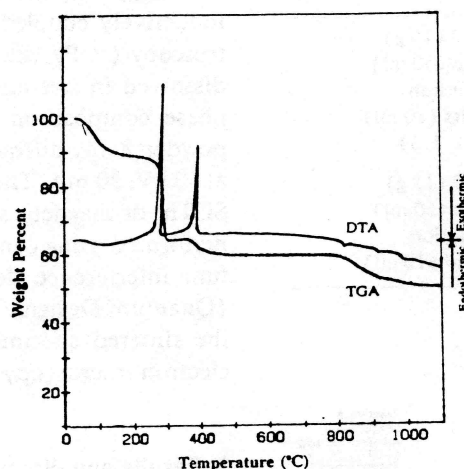


Fig. 3. TGA/DTA thermogram of oxalate precursor powder.

Thermogravimetric studies in air at a heating rate of  $5^{\circ}\text{C}/\text{min}$  (fig. 3) indicate a loss of water at a temperature below  $200^{\circ}\text{C}$ , followed by the decomposition of  $\text{CuC}_2\text{O}_4$  to  $\text{CuO}$  between  $200$  and  $300^{\circ}\text{C}$ . The decomposition of anhydrous copper oxalate leads to the formation of elemental copper and  $\text{CO}_2$ , after which copper is oxidized to  $\text{CuO}$  [49]. A slight weight gain after the second weight loss step in the TGA curve is due to the oxidation of elemental copper to  $\text{CuO}$ . The two-step decomposition of yttrium oxalate to  $\text{Y}_2\text{O}_3$  via  $\text{Y}_2(\text{CO}_3)_3$  occurred in the range between  $300$  and  $450^{\circ}\text{C}$ , overlapped by the transformation of barium oxalate into barium carbonate.

These decompositions agree with the weight changes observed for the individual oxalates and are in correspondence with the exothermic peaks in the DTA curve. Barium carbonate starts to decompose to barium oxide at  $750^{\circ}\text{C}$  and completes around  $850^{\circ}\text{C}$ . These results indicate that on attaining a temperature of  $550^{\circ}\text{C}$  for nanosize precursor oxalate powder, the oxalates are transformed into a mixture of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$ . The decomposition of  $\text{BaCO}_3$  to  $\text{BaO}$  started around  $750^{\circ}\text{C}$  for the nanoparticles of oxalate precursor powder, as compared to  $870^{\circ}\text{C}$  for bulk coprecipitated oxalate precursor and greater than  $1000^{\circ}\text{C}$  for pure barium carbonate [27]. The reduction in decomposition temperature in the case of nanometer sized particles may be due to very high

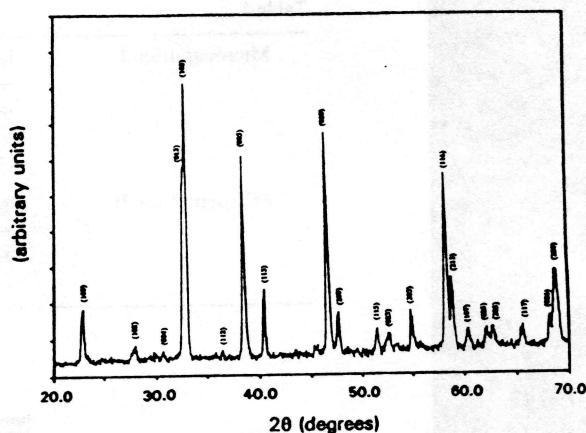


Fig. 4. X-ray diffraction pattern of the sample sintered at  $930^{\circ}\text{C}$ .

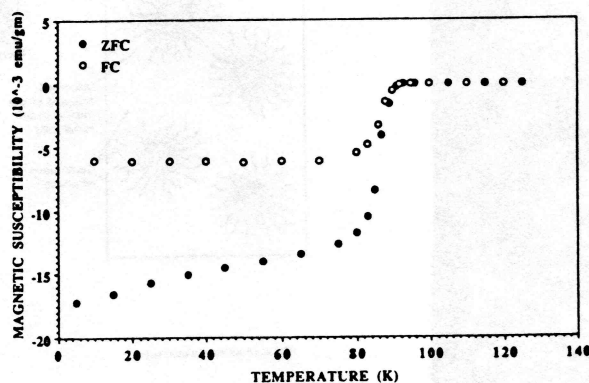


Fig. 5. dc magnetic susceptibility as a function of temperature of the sample sintered at  $930^{\circ}\text{C}$ .

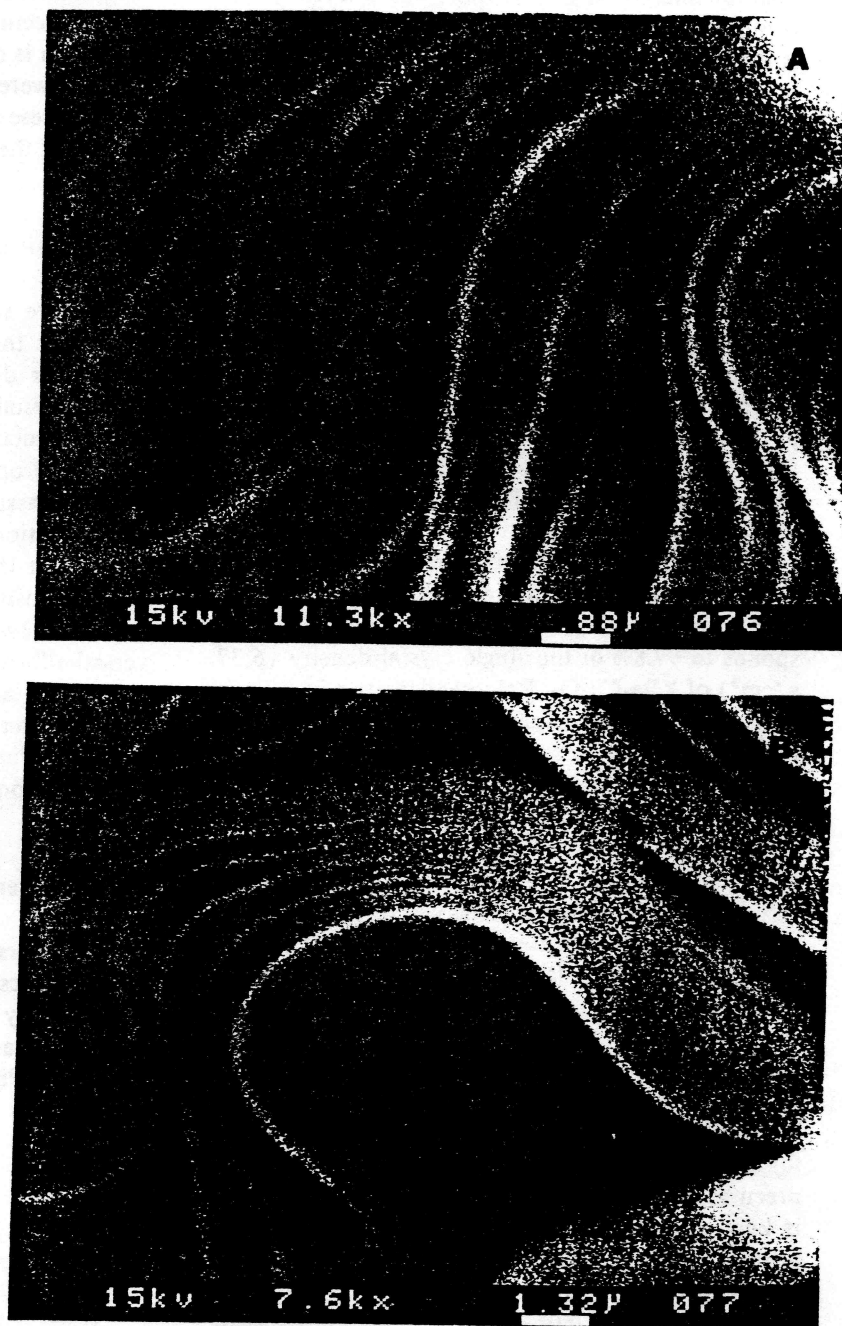


Fig. 6. SEM micrographs of sintered sample.

surface pressure induced by the curvature.

The dehydrated precursor oxalate powder was calcined at 800°C for 12 h in air. Energy dispersive X-

ray analysis (EDAX) of the calcined powder confirms the presence of all the metal species almost in the same cationic ratio as were initially used because

of the complete precipitation of cations as oxalates from the acetic acid medium. The elemental composition analysis at several spots was uniform which is indicative of a highly homogeneous material. This is due to the fact that all the cations are uniformly mixed and the scale of homogeneity is limited by the size (3–12 nm) of the precursor powder which constitutes all the metal oxalates in the required cationic ratio in each particle unit. Peaks pertaining to all the cations were present in the EDAX spectrum. The ICP/AES analysis further confirms that all the cations were present in a perfect cationic ratio in the calcined powder.

X-ray diffraction spectrum of the sintered sample (fig. 4) shows only peaks for the orthorhombic superconducting phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . No impurity peaks were observed in the diffraction spectra. All the diffraction peaks can be accounted for by an orthorhombic unit cell with  $a=3.818 \text{ \AA}$ ,  $b=3.881 \text{ \AA}$  and  $c=11.679 \text{ \AA}$ .

The density of the sintered pellets was measured by the Archimedes method by employing isooctane. The bulk density of the sintered material corresponds to 97.8% of the single crystal density ( $6.37 \text{ g/cm}^3$ ) of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . Relative density of > 97% is quite remarkable for superconductors sintered under ambient pressure.

The superconducting transition temperature was determined (using SQUID magnetometer) by cooling the sample in zero field and warming it up in a field of 20 G. The temperature dependence of dc susceptibility of the sintered pellet was measured down to 4.8 K. The microemulsion derived material exhibits substantially large zero-field (diamagnetic shielding) and field cooled (flux expulsion) signals (fig. 5). A  $T_c$  of 92 K was observed. The diamagnetization corrected value of ZFC signal (Meissner shielding) is > 93% (93.2%) of that expected from an ideal sample ( $-1/4\pi$ ). The corresponding value for the material prepared from bulk coprecipitated precursors is only 53% [28]. The Meissner fraction is known to depend on the applied field. The dependence is particularly strong for the low applied fields and the Meissner fraction approaches 100% for an applied field of 0.01 G. Note that the relatively high value of Meissner fraction (93%) that we obtained corresponds to a relatively large field (20 G).

The resulting morphology of the sintered pellet is

shown in figs. 6A and 6B. Remarkably dense material with minimum porosity can be observed in fig. 6. These micrographs were taken at different areas of the specimen. Highly dense, laminar-like grain formation is due to the fact that ultrafine precursor powders were used for the fabrication of these materials. These results are consistent with the very high density of the sintered material.

#### 4. Conclusions

We have shown that microemulsions are novel media for the synthesis of precursor materials of nanometer dimensions. These ultrafine precursor powders result in highly dense, potentially fully dense, superconducting materials with strong Meissner signal after proper processing. Perfect homogeneity of cations is assured by the extremely small dimension of the reaction vessel ( $\approx 5\text{--}25 \text{ nm}$ ). These results indicate that these materials may have very critical current density. The precise control of size and shape of the nanosize domains makes these systems very versatile for the preparation of ultrafine powders of desired size and shape with narrow size distribution of nanometer dimensions. Such materials would be useful for studying the grain size dependence of various superconducting properties.

#### Acknowledgement

The authors thank Mr. W.W. Kim and Dr. J.S. Kim of the Physics Department for their help in magnetic susceptibility measurements and Mr. Guy Latore for TGA/DTA analysis. Financial support from EPRI (Grant #RP8009 22) is gratefully acknowledged.

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