

Preparation of Bi-Pb-Sr-Ca-Cu-O oxide superconductors by coprecipitation of nanosize oxalate precursor powders in the aqueous core of water-in-oil microemulsions

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We describe a new technique for the synthesis of ultrahomogeneous nanoparticles of precursor oxalate powder by coprecipitation in the aqueous core of a water-in-oil microemulsion for the preparation of Bi-Pb-Sr-Ca-Cu-O (2223) oxide superconductor. This process ensures a uniform mixing of metal cations down to a scale of at least 10 nm. This finely dispersed precursor powder results in phase pure (2223) oxide superconductor after proper heat treatment.

Since the discovery of superconductivity in the Bi-Sr-Ca-Cu-O system,¹ many efforts have been focused on the preparation of monophasic (2223) high T_c superconductor. However, it is extremely difficult to synthesize the 105–115 K single-phase superconductor. There are four methods used to promote the formation of the high T_c phase: doping with Pb,^{2–6} careful control of the sintering temperature and prolonged (> 100 h) heat treatment,⁷ sintering under the reduced oxygen pressure,^{8,9} and the modification of the starting nominal composition.^{9,10} To date, the overall mechanism for the formation and promotion of the 2223 phase is not well understood.

In order to achieve an acceptable level of homogeneity, wet chemical techniques such as coprecipitation,¹¹ freeze drying,¹² and amorphous citrate process¹³ have been used. These methods are, therefore, superior to commonly used solid-state reaction techniques. Oxalate coprecipitation has been used frequently for the preparation of various superconductive series.^{14–17} Most recently, coprecipitation of Bi-based precursor oxalates from an aqueous acetic acid medium has been reported.¹⁸

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, and the morphology of the precursor powder and the heat treatment conditions are critical to obtain the desired microstructure. A wet chemical synthesis process results in a better homogeneous material compared to 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 an aqueous core of water-in-oil (w/o) microemulsion as the nanoreactor for the chemical reaction offers this opportunity.^{19–21} Microemulsions are thermodynamically stable isotropic dispersions consisting of the nanosize domains of oil and/or water stabilized by an interfacial film of a surface active agent. The precise control of the size and stability of the nanostructure domains provide a novel media for the preparation of mesoscopic particles of desired size or shape with a narrow size distribution. The precipitation inside the nanosize domains (5–25 nm) of w/o microemulsion would result in nanoparticles of uniform size distribution and of better homogeneity when compared to bulk aqueous precipitation,

which results in uncontrolled nucleation and growth. We have successfully demonstrated the preparation of ultrafine precursor powder by coprecipitation in the aqueous core of w/o microemulsion for the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor of almost theoretical density and > 90% of ideal Meissner shielding recently.^{22,23} In this letter we report the synthesis of nanoparticles of Bi-Pb-Sr-Ca-Cu oxalate precursor powder by the coprecipitation in the nanosize domains of w/o microemulsion, which results in Bi-Pb-Sr-Ca-Cu-O (2223) superconductor after the proper heat treatment.

All the chemicals [Bi_2O_3 , $\text{Pb}(\text{CH}_3\text{COO})_2$, SrCO_3 , CaCO_3 , and $\text{Cu}(\text{CH}_3\text{COO})_2$] used were of high purity (> 99.9%). Acetic acid and cyclohexane were of reagent grade. Surfactant Igepal CO-430, nonylphenoxypoly (ethyleneoxy) ethanol, $(\text{C}_2\text{H}_4\text{O})_4\text{C}_{15}\text{H}_{24}\text{O}$, was of a commercial grade. Bi_2O_3 , $\text{Pb}(\text{CH}_3\text{COO})_2$, SrCO_3 , CaCO_3 , and $\text{Cu}(\text{CH}_3\text{COO})_2$ were dissolved in 25:75 (v/v) acetic acid/water mixture in the molar ratio of Bi:Pb:Sr:Ca:Cu::1.84:0.34:1.91:2.03:3.06 using 0.0368 M of Bi^{3+} . This solution was heated to dryness and the residue was redissolved in 50/50 acetic acid/water mixture. A clear blue solution was obtained. Oxalic acid in 10% excess of the 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 as the aqueous phase. The nanosize domains (aqueous core of w/o microemulsions) frequently collide and move apart rapidly.²⁴ This allows the reacting species to come in contact when a microemulsion containing all the metal salts is mixed with another microemulsion containing precipitating agent. Since both the microemulsions have the same surfactant: hydrocarbon: aqueous phase (differing only the nature of salt dissolved), the microemulsion does not get destabilized on mixing them. The steric barrier provided by the surfactant monolayer restricts the growth of precipitated oxalate particles and hinders intergrain coagulation. Serial precipitation of cation (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). Compositions of both microemulsions are given in

TABLE I. Composition of microemulsions.

Microemulsion I	Igepal Co-430 (15 g) + cyclohexane (50 ml) +aqueous solution of metal salts (10 ml).
Microemulsion II	Igepal Co-430 (15 g) + cyclohexane (50 ml) +aqueous solution of oxalic acid (10 ml).

Table I. The cations precipitate as Bi-Pb-Sr-Ca-Cu oxalate particles by the reaction with oxalic acid within the aqueous core of the microemulsion. A schematic representation of the process and of w/o microemulsion is shown in Fig. 1.

The precipitate was separated in a superspeed centrifuge at 5000 rpm for 10 min. This precipitate was washed repeatedly with a 1:1 methanol:chloroform mixture to remove all the surfactant. A small drop of this suspension was placed on the transmission electron microscopy (TEM) grid for particle size analysis. The JEOL-200 CX was used for TEM studies. Precipitate was dried at 100 °C in air. Figure 2 shows the transmission electron micrograph of the precursor oxalate powder. It can be seen from TEM micrograph that these particles are fairly monodispersed with a size range of 2–6 nm. However, few larger loose aggregates were also observed which may be due to aggregation during the washing step.

The thermogravimetric measurements were performed on coprecipitated oxalate precursor powder in air atmosphere at a heating rate of 10 °C/min by a DuPont (TGA/DTA) 900 Series Instrument. The rather dramatic loss around 300 °C is caused by the conversion of copper and bismuth oxalates to CuO and Bi₂O₃. The gradual weight loss above 500 °C is due to the loss of CO₂ from CaCO₃ and SrCO₃. Two exothermic peaks in DTA thermogram between 200 and 400 °C are in good agreement with sharp weight loss in TGA curve which is indicative of the loss of organic moieties.

The dehydrated precursor oxalate powder was calcined

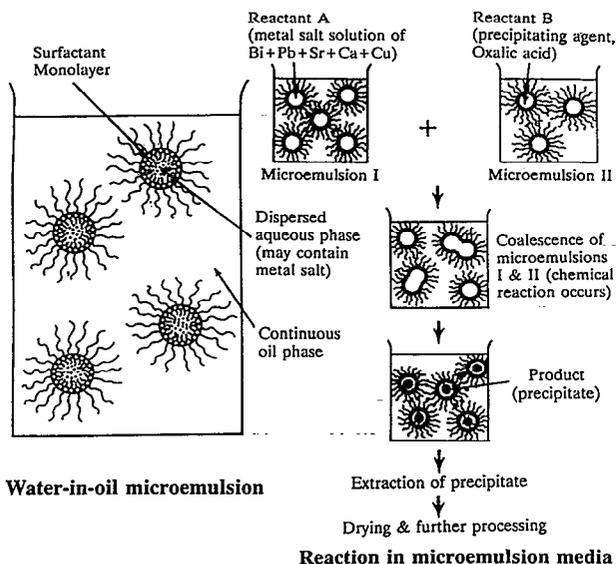


FIG. 1. Schematic of w/o microemulsion and of the reaction mechanism.



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

at 800 °C for 12 h. Energy dispersive x-ray analysis of the 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 the metal oxalates from acetic acid medium.¹⁸ The elemental composition analysis at several spots was uniform which is indicative of 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 (2–6 nm) of the precursor powder which constitutes all the metal oxalates in the required cationic ratio in each single particle unit.

The calcined powder was pressed into pellet of 6 mm diam under a static pressure of 120 MPa and sintered for 96 h (unoptimized) at 850 °C in air in a tube furnace. The magnetization data were recorded with commercial superconducting quantum interference device magnetometer (quantum design). The dc magnetic susceptibility measurement as a function of temperature are reported in Fig. 3(a). An abrupt change in the magnetization curve was observed at 112 K marking the transition to superconducting state. No step around 80 K was observed in the magnetization curve, which is due to the presence of 2212 phase. The zero field cooled signal (diamagnetic shielding) corresponds to 93% of the Meissner shielding expected from an ideal sample ($-1/4\pi$). X-ray powder diffraction spectra were obtained on Philips x-ray diffractometer using CuK α radiation at 40 KV, 20 mA. Figure 3(b) shows the x-ray diffraction pattern of the sample after 96 h of sintering at 840 °C. The series characteristic diffraction peaks of 110 K phase; 002, 0010, at $2\theta=4.8^\circ$ and 23.9° are seen in the diffractogram. The 80 and 20 K phases, whose characteristic peaks are at $2\theta=5.7^\circ$ and 7.2° , respectively, are not observed, but weak additional peaks are observed at 2θ

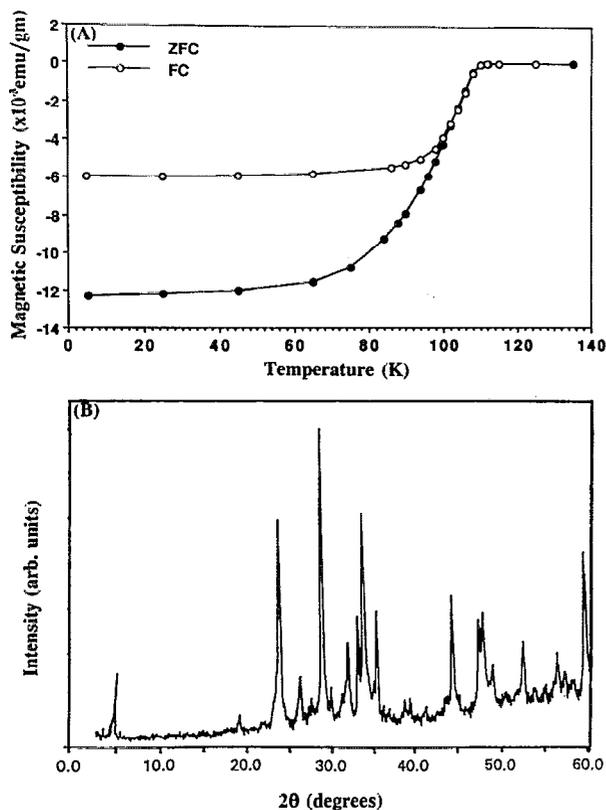


FIG. 3. (a) dc-magnetic susceptibility as a function of temperature of sample sintered at 840 °C. (b) x-ray diffraction pattern of the sample sintered at 840 °C.

$\approx 30^\circ\text{--}31^\circ$. These results unambiguously indicate that almost phase pure 2223 oxide superconductor phase was achieved.

A larger grain growth and densification can be expected in the sintered sample due to the appearance of liquid phase during sintering or due to the ultrafine nature of the precursor powder. Large lamellar like grains were formed and highly dense layered material results after sintering. Density of sintered sample, as determined by helium pycnometry, is 97% of theoretical value.

In summary, we have shown that microemulsion is a novel system for the synthesis of nanoparticles of oxalate precursor which after proper heat treatment results in almost phase pure 2223 oxide superconductor of almost theoretical density with significantly higher Meissner effect.

Perfect chemical homogeneity is assured due to the very small size (5–25 nm) of the reaction vehicle. Further optimization of calcination and sintering condition should result in better oxide ceramic material with superior superconducting and mechanical properties.

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