Mat. Res. Bull., Vol. 24, pp. 1069-1076, 1989. Printed in the USA. 0025-5408/89 \$3.00 + .00 Copyright (c) 1989 Pergamon Press plc.

## SYNTHESIS OF SUPERCONDUCTING OXIDES BY AEROSOL PYROLYSIS OF METAL-EDTA SOLUTIONS

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(Received June 6, 1989; Communicated by A.W. Sleight)

## ABSTRACT

Superconducting oxides in the form of powders or coatings are synthesized from aqueous metal ethylenediamine-tetraacetic acid (EDTA) solutions. The solutions are dispersed ultrasonically to form an aerosol of extremely fine droplets in an oxygen carrier stream. The solution aerosol is passed through a tubular high temperature furnace and converted into submicron size oxide particles which are collected by a hot ceramic filter or by electrostatic precipitation.

MATERIAL INDEX: Superconductors, yttrium, bismuth, copper, oxides

# Introduction

The discovery of high temperature superconductivity in certain copper-based oxide systems has created a need for synthesizing these materials in bulk powder form or as large-scale surface coatings. Currently, these materials are made largely by the conventional ceramic sintering technique which may require several sintering/regrinding cycles to obtain a single phase

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product. This method suffers from the fact that it is a batch process and therefore very time consuming. Among the means to form superconducting oxide films, sputtering and evaporation techniques are largely applied for electronic device fabrication. Plasma deposition, chemical vapor deposition and sol-gel processes are being investigated for applying large-area superconducting oxide films and are in various stages of development.

The authors recently demonstrated an aerosol-pyrolysis process for making bulk superconducting oxide powder or coatings using an aqueous nitrate solution of the metals of interest, specifically YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>(1). Concurrently, Kodas *et al.* (2) developed a similar aerosol flow process for fabricating superconducting ceramics. When we tried to extend the aerosol process to other metal constituents, such as Bi and Tl, the nitrate solution had to be strongly acidified with nitric acid in order to prevent precipitation of oxynitrates. High acidity of the solution is undesirable for two reasons: a) it produces a high concentration of various nitric oxides (NO<sub>x</sub>) in the reactor exhaust which may react with the oxide particles at lower temperatures to reform nitrates; b) it may corrode various construction materials of the reaction system and thereby contaminate the product.

In sharp contrast to the high acidity frequently needed to keep metal nitrates in solution, near-neutral aqueous solutions of the metals of interest can be achieved by employing soluble metal complexes derived from ethylenediamine-tetraacetic acid  $[H_A(EDTA)]$  having structure I:

$$\frac{HOOC-CH_2}{HOOC-CH_2} > N - CH_2 - CH_2 - N < CH_2 - COOH$$

The deprotonated derivatives of  $H_4(EDTA)$  are powerful chelating agents for many different divalent and polyvalent metal cations in solution (3). Usually all four of the acidic hydrogens of  $H_4(EDTA)$  are lost during chelation and the metal forms coordinate-covalent bonds with the two

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<sup>\*.</sup> Ethylenediamine-tetraacetic acid is often referred to loosely as "EDTA". However, the designation H<sub>4</sub>(EDTA) is to be preferred since it emphasizes the tetrabasic nature of the acid and forms the basis for shorthand representations of deprotonated forms of the compound and its metal complexes.

nitrogen atoms of I. For example, the soluble cupric chelate of EDTA has the structure II. It is important to note that chelates of type II are anions and require the presence of positively charged cations in solution for overall charge balance. We have chosen ammonium  $(NH_4^+)$  as the neutralizing cation since it is destroyed during subsequent pyrolysis and hence does not appear in the final ceramic products, as would alternate cations such as Na<sup>+</sup> or K<sup>+</sup>.



A number of experimental methods can be employed for the preparation of ammonium EDTA metal chelates directly in solution. However, many of these give a solution which contains not only the desired metal EDTA complex but also undesirable ionic byproducts. Hence, we have employed only those methods which are free of byproducts other than water or volatile carbon dioxide. One set of reactions employed is represented by reactions (1) and (2) where M denotes a divalent metal.

$$H_{4}(EDTA) + 2NH_{4}OH + (NH_{4})_{2}H_{2}(EDTA) + 2 H_{2}O$$
(1)

$$\mathbb{M}(\mathrm{OH})_{2} + (\mathrm{NH}_{4})_{2}\mathbb{H}_{2}(\mathrm{EDTA}) \rightarrow (\mathrm{NH}_{4})_{2}\mathbb{M}(\mathrm{EDTA}) + 2\mathbb{H}_{2}0$$
(2)

$$\mathbb{M}(\mathbb{CO}_3) + (\mathbb{NH}_4)_2 \mathbb{H}_2(\mathbb{E}DTA) \rightarrow (\mathbb{NH}_4)_2 \mathbb{M}(\mathbb{E}DTA) + \mathbb{CO}_2^+ \mathbb{H}_2^0$$
(3)

The nearly-insoluble parent acid  $H_4(EDTA)$  is suspended and stirred in water and then half neutralized with the stoichiometric amount of dilute NH<sub>4</sub>OH. The resulting diammonium salt dissolves completely. Freshly precipitated, washed metal hydroxide is then added in stoichiometric quantity and stirred with heating until a clear solution is obtained. Reaction (3) shows that the corresponding carbonate can sometimes be substituted for the hydroxide. Reactions (1) through (3) are formulated for divalent metals. Similar reactions can be written for trivalent metals. Trivalent metals generally give the compound  $(NH_4)M(EDTA)$  which dissociates in solution to  $NH_4^+$  and  $M(EDTA)^-$  ions. However we find that bismuth apparently gives the soluble compound  $(NH_4)_2Bi(OH)(EDTA)$  near neutral pH values.

In the work described here the EDTA solutions of Ba, Ca, and Sr were prepared by reactions (1) and (3). All other metal EDTA solutions were prepared by reactions (1) and (2). All starting materials were of reagent grade quality. Insoluble hydroxides employed in reaction (2) were prepared from the corresponding nitrates by precipitation with  $NH_4OH$ except for Cu(OH)<sub>2</sub> where it was necessary to use NaOH to prevent formation of cupric-ammonia complexes. Any Na<sup>+</sup> ion adhering to the precipited Cu(OH)<sub>2</sub> is removed by repeated washing with water.

Solutions of individual ammonium metal EDTA compounds were prepared separately and then combined in a volumetric flask in the proper stoichiometric proportions to give the desired oxide superconductor upon decomposition. In no case was there evidence for chemical interaction between the dissolved species in the combined solution at room temperature (i.e. no precipitation or color change).

The solutions were dispersed with a modified DeVilbis<sup>\*</sup> Ultra-Neb 99<sup>TM</sup> ultrasonic nebulizer. The aerosol was carried with oxygen through a tubular furnace where the solution droplets converted into mixed metal oxide particles through a series of processes that include flash evaporation of water, and decomposition and oxidation of the metal EDTA compounds. The oxide particles were collected on a hot PTFE filter or on a hot electrostatic precipitator plate.

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### EDTA SOLUTIONS

### <u>Results</u>

The preparation of mixed oxides by the pyrolysis of aerosols of metal EDTA solutions was demonstrated with Y-Ba-Cu and Bi-Sr-Ca-Cu superconducting oxide materials.

The mixed oxide  $YBa_2Cu_3O_{7-x}$  was synthesized from solutions of Y, Ba and Cu EDTA which were individually prepared and mixed in the molar ratio 1:2:3 for Y, Ba, and Cu to give a total metal concentration of 0.06 mol/l.

The solution aerosol was decomposed at a maximum reactor temperature of 950°C and at a flow rate of 4 l/min. The residence time of the particles in the reactor was about 2 seconds. The particles were collected on a PTFE micropore filter. The x-ray diffraction diagram of the as-processed powder is shown in Fig. 1 and agrees with the results of published information (4) on tetragonal  $YBa_2Cu_3O_{7-x}$ .

A mixed oxide of the composition  $BiCaSrCu_2O_x$  was prepared from the combined EDTA solutions of the individual metals. The total metal concentration had a molarity of 0.05. The reactor temperature was held at about 900°C and the flowrate was held at 4 l/min. The electrostatically collected powder was subsequently annealed at 850°C in oxygen for about 12 hours. An X-ray diffraction spectrum of this material is shown in Fig. 2. The spectrum agrees with that reported by Maeda *et al.* (5) for the same composition.

The powder prepared from metal EDTA solutions contained a significantly higher level of carbon, presumably as carbonate, than powder made from nitrate solutions. A LECO analysis of total carbon in  $BiSrCaCu_2O_x$  showed 1.4 weight % carbon compared to only 0.18% C for nitrate produced powder. A portion of the carbon may have been added by exposure to ambient air.

A typical SEM micrograph of aerosol pyrolyzed powder is shown in Figure 3. Single grain growth is evident from the faceting of many particles. The average particle size of a statistically significant number of particles was found to be  $0.5 \pm 0.1 \ \mu m$ .



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1µm ←→

Fig. 3 SEM micrograph of as-processed  $YBa_2Cu_3O_{7-x}$  prepared from an EDTA solution.

## Conclusions

Rare earth and bismuth containing superconducting oxide powders can be synthesized by aerosol pyrolysis of aqueous solutions of the constituent metals in ethylenediamine-tetraacetic acid (EDTA). The EDTA solutions have near neutral pH in contrast to the equivalent acidic nitrate solutions. The submicrometer size particles have a narrow size distribution which facilitates their sintering and densification at temperatures below 900°C. Additional work is needed to reduce the residual carbon level in the product.

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