

Preparation of Phase Pure Cuprate Superconductors via The Modification of Sol-Gel Method

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Abstract : A modification of the sol-gel method to obtain phase pure superconducting oxides is described. The method starts from organic salts of yttrium, barium and copper, such as acetates, and avoids the sudden and uncontrollable decomposition of the organic fraction which occurs if nitrates are used as starting materials. The aqueous solution obtained with citric acid in an alkaline medium is concentrated under vacuum. The solid so prepared is decomposed at about 300°C thus giving an oxide precursor containing well dispersed yttrium, barium and copper. Pyrolysis at 850 - 920°C followed by oxygen annealing gives the superconducting orthorhombic 123 phase. The results of TGA/DTA of the precursor, as well as XRD, electrical and magnetic property measurements on the pyrolysis products are presented and discussed.

Key words : Cuprate superconductors, Sol-Gel, XRD, Phase purity, Electrical resistance

1. Introduction

The sol-gel process offers new approaches to the synthesis of oxide materials. Starting from molecular precursors, an oxide network is obtained via inorganic polymerization reactions.¹⁾ These reactions mainly occur in solutions and the term "sol-gel processing" is often broadly used to describe the synthesis of inorganic oxides by wet chemical methods. It offers many advantages compared to the conventional powder routes, such as lower temperature processing or better homogeneity for multicomponent materials. The rheological properties of sols and gels allow the fabrication of fibers or films by such techniques as spinning or dip coating.^{2, 3)} However, sol-gel syntheses for films and fibres have been slow in coming because of the large shrinkages that result from solvent losses. Two different approaches to sol-gel preparation of cuprate oxides have been made: non-aqueous and aqueous based routes.⁴⁻¹⁰⁾ In both cases, the reaction can be described as follows: (i) Hydroxylation of the precursor leading the formation of M-OH bonds; the hydroxylation

of inorganic precursor is performed via pH modification of the aqueous solution leading to the protonation of anionic oxo-ions or the deprotonation of cationic aquo-ions. The hydroxylation of alkoxides is simply performed via hydrolysis by adding water. (ii) Condensation: a polycondensation process follows the hydroxylation reaction leading to the departure of a water molecule. In both cases, hydroxy or oxygen bridges are formed leading to condensed species. At the end of the process all oxygen atoms are bridging oxygens and a hydrated oxide network is obtained.

Different chemical approaches may be required to obtain superconducting powders with high phase purity, small particle size, and lower heat treatment temperatures. A key requirement for the practical application of this and related high-T_c oxides is a better method for the fabrication of these materials in useful final forms. Simple but rather crude preparation methods are most common, using conventional ceramic processing methods, such as repeated grinding and calcination of oxides and

carbonates, although these methods are not ideal. Several disadvantages are evident, such as inhomogeneity, non-uniformity of particle size and shape, high impurity contents, lack of reproducibility, necessity of repeated processing because of incomplete synthesis and low current densities.

Increasing efforts have been made to obtain a homogeneous precursor with good stoichiometry and well-interspersed elements before high-temperature calcination.¹¹⁻²²⁾ Several routes have been developed to reach this goal, such as coprecipitation of carbonates or oxalates, sol-gel, and freeze-drying. These methods, however, still have some drawbacks. The coprecipitation route suffers from impurities from the precipitating agents, incompleteness, non-uniformity and material loss during washing. The sol-gel route has many preparation steps, all critical for the properties of the final material, it requires expensive chemicals and is time consuming. Major problems in freeze-drying are associated with melting before drying and salt dissolution in residual water of hydration before decomposition, which may cause inhomogeneity in the calcined sample. However, to our knowledge, all the above-mentioned preparations used nitrates of yttrium, barium and copper. This is probably not the best choice because problems may arise, particularly in scaling-up, because nitrates in the presence of an organic substance can give rise to an abrupt and uncontrolled decomposition of the organic material, eventually leading to spontaneous combustion in the vessel in which the solution is being concentrated. This observation may be particularly true in the presence of copper salts. The most versatile precursors for the sol-gel synthesis of oxides are undoubtedly metal oxides which are very reactive toward nucleophilic reagents such as water. These alkoxides appear to be much more reactive than silicon alkoxides. They must be handled with great care in a dry environment and are often stabilized via chemical modification. This high chemical reactivity is due to the lower electronegativity of the metal as compared with silicon, and the metal atoms ability to

exhibit several coordination states. As a result of the latter property, coordination expansion spontaneously occurs when the metal alkoxide reacts with water.

The properties of a gel and its response to heat treatment are very sensitive to the structure already created during the sol stage. Therefore the formation of colloidal aggregates often determines the main properties of resulting powder and its ability for the extent to which the powder can be sintered. Monodispersed transition metal oxides colloids are currently synthesized which can exhibit anisotropic shapes. Particle-particle interactions then lead to the formation of anisotropic aggregates in which all individual particles are mutually oriented. These ordered aggregates can lead to anisotropic coatings that behaves as host structures for intercalation. In efforts to reduce cracking, fine porosity and residual carbon in films produced, systems containing copper should be decomposed with caution, preferably in a very thin layer and using small quantities. Best results are also obtained by decomposition of the citrate at the lowest possible temperature. To obtain a smooth and controlled decomposition by the amorphous citrate route, acetates are used as starting salts instead of nitrates.

2. Experimental

Reagent grade metal acetates were obtained from commercial sources (Aldrich and Sigma) and analysed to determine their levels of hydrated water. Yttrium and copper acetates were converted to the corresponding oxides at 950°C in flowing oxygen. The amount of water was then determined. The barium content in barium acetate was determined by a precipitation technique. Yttrium, barium and copper acetate solutions were mixed with citric acid and neutralized with NH₄OH. The solutions so obtained were mixed together with agar, producing a deep blue solution which was concentrated in a revolving flask under vacuum at about 50-60°C for about 30min, until a viscous

slurry was obtained. The slurry was finally dried under vacuum to give a light blue powder. This was slowly decomposed in air at temperatures below 300°C until no exothermic effect was measured with a thermocouple dipped in the powder. The samples were calcined at various temperatures. After calcination sample was pressed into a pellet and sintered at 850 - 920°C and post oxygen annealing was done at 550°C under flowing oxygen for five hours, followed by slow cooling to room temperature.

Thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer DSC-2C/TGS-2 TADS system. X-ray diffraction patterns of the intermediates (at different stages of heat treatment), final products were obtained using a Rigaku D/max-B X-ray diffractometer. The data were compared with a CD-ROM powder diffraction file compiled by JCPDS center for diffraction data. Magnetic susceptibility data for a temperature range in a magnetic field lower than 0.5 Tesla were measured using a SQUID (superconducting quantum interface device) magnetometer. Resistivity data were obtained using the four probe method on pressed and sintered pellet.

3. Results and Discussion

Analysis of results showed the starting metal acetate formula to be $Y(CH_3COO)_3 \cdot 3H_2O$, $Cu(CH_3COO)_2 \cdot 0.8H_2O$ and $Ba(CH_3COO)_2$. The precursor solution was prepared from the metal acetate salts dissolved in distilled water. A typical procedure involves mixing appropriate amounts of yttrium acetate trihydrate, barium acetate and copper acetate monohydrate in 89.5 mol% of distilled water. The solution was heated to 60°C to dissolve the solids. Citric acid and Agar was then added slowly while stirring. The blue solution was concentrated and a viscous slurry was obtained. The precursor was blue, homogeneous, clear, glassy solids. On heating to 300-400°C it darkened and shrank in volume without melting or foaming; the product was black, apparently still homogeneous, glassy solids.

The sol-gel solution becomes viscous without precipitation, indicating a very homogeneous mixture was made. The gel is held together by weak inter-particle forces, which are evident by breakdown of the gel under any kind of shearing process, such as shaking or spraying. The gel is reformed after shearing and remains stable for months. The viscous solution can be made suitable for spinning, spraying, or dipping processes. Analysis of the precursor by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in Figure 1 shows that nearly 99% of the total weight loss occurred below 250°C.

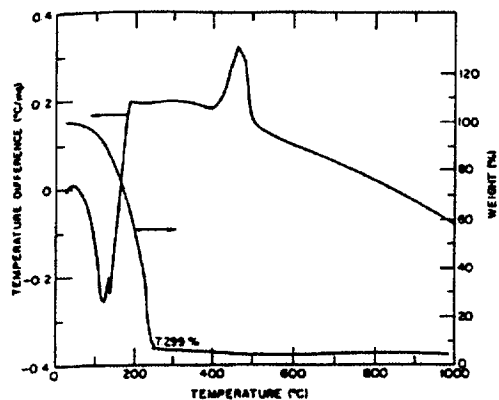


Figure 1. TGA/DTA curve for the citrate 1-2-3 precursor

Most of this weight loss is due to evaporation of water, as indicated by the endothermic peaks in the DTA below and near 200°C. Above 200°C, the acetates began to decompose. Copper acetate was evident even at 200°C by the formation of a rusty-red film colour that indicates the reduction of copper(+2) to copper(+1) and possibly copper metal. The powder turned black at 250 - 300°C, indicating oxidation back to copper(+2) oxide. Yttrium and barium acetate decomposition occurred between 300-500°C, as indicated by the large exotherms in the DTA. Both TGA and DTA results showed that nearly all organics were removed by 500°C as no further weight loss was seen. $BaCO_3$ was however still present and did not decompose until higher temperatures.

Figure 2 shows the XRD patterns of the solid

pyrolysis products of the precursor after extended heating at different temperatures from 500-920°C. The precursor powder is amorphous at room temperature. At 400°C three main phases appear: Y_2O_3 , CuO , $BaCO_3$, and it is apparent that a mixture of CuO , Y_2O_3 and $BaCO_3$ is present by at least 500°C and the orthorhombic phase of the $YBa_2Cu_3O_7$ starts to appear at 800°C. This phase was fully developed after heating at 920°C for 5 hours. The formation of $BaCO_3$ as an intermediate and its subsequent thermal decomposition to BaO explains the gradual weight loss at 600-800°C observed by TGA.

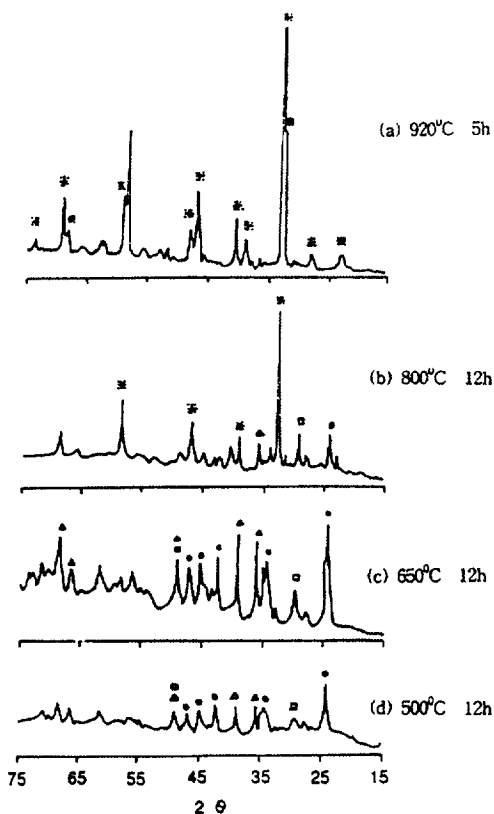


Figure 2. XRD patterns of the citrate precursor after calcination at different temperatures (\square ; Y_2O_3 , \circ ; $BaCO_3$, Δ ; CuO , \circ ; $YBa_2Cu_3O_7$) (a) 920°C 5h, (b) 800°C 12h, (c) 650°C 12h, (d) 500°C 12h

The magnetic susceptibility measurements of the powder obtained from the pyrolysis at 920°C indicated a $T(\text{onset})$ of 90K whereas electrical

conductivity measurements of a pressed pellet of this powder after annealing in O_2 indicated a $T(\text{onset})$ of 97K (Figure 3). Figure shows metallic behaviour with a sharp drop to the superconducting state. These results are consistent with those of the previous studies of 1-2-3 superconductor samples derived from solid state reaction.

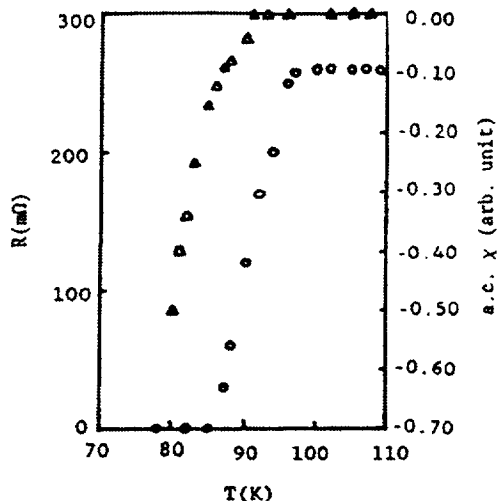


Figure 3. Electrical resistance and magnetic susceptibility on the precursor derived 1-2-3 superconductor (\circ ; electrical resistance, Δ ; magnetic susceptibility)

4. Conclusions

The preparation of cuprate superconducting $YBa_2Cu_3O_7$ compounds was attempted through the modification of sol-gel method using an aqueous solution of metal acetates containing a citric acid. This process produces high phase purity oxide superconducting powders. The method also gives atomically mixed precursor, generalization to other superconductor ceramics and energy efficiency without many of the disadvantages, such as long processing time, unstable precursors and labor intensity. The route leads to a precursor obtained at about 300°C containing well interspersed yttrium, barium, and copper. Because of the lack of nitrates in the dedicated sample the

decomposition may be performed in a controlled way. The $\text{YBa}_2\text{Cu}_3\text{O}_7$ compound was already formed at about 700°C . The compound sintered at 920°C followed by oxygen annealing has good superconducting properties.

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