Thermochimica Acta, 174 (1991) 169–183
Elsevier Science Publishers B.V., Amsterdam

CHEMICAL PROCESSING OF THE HIGH-TEMPERATURE SUPERCONDUCTOR $Ba_2YCu_3O_{7-\delta}$ THROUGH SOLUTION ROUTES AND THERMAL BEHAVIOUR ON PYROLYSIS

SHIN-ICHI HIRANO * and TAKASHI HAYASHI

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464 (Japan)

(Received 24 October 1989)

ABSTRACT

This review describes features of chemical processing methods, through solutions and the thermal behaviour of the resulting precursors, for synthesizing the high-temperature superconductor $Ba_2YCu_3O_{7-\delta}$. The sol–gel and coprecipitation methods have received much attention in the preparation of chemically homogeneous superconductors having desired shapes at relatively mild temperatures.

Chemically homogeneous powders and thin films having the preferred orientation of single phase $Ba_2YCu_3O_{7-\delta}$ can be successfully prepared below 800 ° C by the sol–gel method with metal alkoxides. Coprecipitation through citrates offers better compositional control and mixing at the molecular level in solutions, compared with oxalate and carbonate methods.

The formation of undesirable residual carbons during pyrolysis of organometallic-derived precursors can be effectively depressed by the utilization of an O_3/O_2 mixture upon rapid heating or by firing in a vacuum.

INTRODUCTION

Since high-temperature superconductors in copper-oxide-based systems have been discovered, various processing methods have been attempted for fabricating bulk oxide superconducting materials, in particular $Ba_2YCu_3O_{7-\delta}$. The most common method is a solid-state reaction process, typically using Y_2O_3, $BaCO_3$ and CuO. In this method, a stoichiometric mixture of starting powders is calcined in order to decompose $BaCO_3$ and then reacted at temperatures slightly below the incongruent melting point of the $Ba_2YCu_3O_{7-\delta}$ phase. In this-solid state reaction process the decomposition reaction of $BaCO_3$ appears to be the rate-limiting step, which reaction requires a relatively high calcination temperature in order to obtain a

---

[*] Author to whom correspondence should be addressed.

significant decomposition rate of the carbonate (viz. 930 ° C). By repeating the grinding and reacting procedures several times, the volume fraction of the $Ba_2YCu_3O_{7-\delta}$ phase can be enhanced and the superconducting characteristics also can be improved. However, local inhomogeneities make it extremely difficult to complete the formation of $Ba_2YCu_3O_{7-\delta}$ as a single phase. The presence of non-superconducting phases or impurities, especially at grain boundaries, would lead to low critical current densities.

The solid-state reaction method is not conducive to the preparation of chemically homogeneous, pure fine particles having a well-controlled morphology for the production of dense ceramics by sintering.

Therefore, particular attention has been paid to the following: coprecipitation methods of nitrates with oxalate, citrate, and carbonate; pyrolysis methods of organic acid salts; and the spray pyrolysis method of nitrate solution. These procedures may afford highly pure and chemically homogeneous particles at relatively lower temperatures. The sol–gel method using organometallic compounds also has many advantages in the preparation of homogeneous superconductors having desired shapes.

A wide variety of solution routes have been shown to yield $Ba_2YCu_3O_{7-\delta}$ powders with superior physical and chemical characteristics as compared with the solid-state-derived powder [1,2].

This review deals with features of chemical processing and thermal behaviour upon pyrolysis for synthesizing the superconducting oxide $Ba_2YCu_3O_{7-\delta}$ through solution methods, in particular the sol–gel method and the coprecipitation method.

THE SOL–GEL METHOD

Advances in ceramic processing have been achieved by the successful application of the sol–gel processing technique. The sol–gel method using metal alkoxides generally offers possibilities for ceramic formations having arbitrary shapes, such as highly homogeneous and pure powders, films and fibers, by controlling the hydrolysis conditions at lower temperatures.

For example, $Ba_2YCu_3O_{7-\delta}$ powders or films can be fabricated by the sol–gel method using metal alkoxides. Murakami et al. [3] have prepared superconducting $Ba_2YCu_3O_{7-\delta}$ powders by hydrolysing $Y(O\text{-}n\text{-}C_4H_9)_3$, $Ba(O\text{-}n\text{-}C_4H_9)_2$ and $Cu(O\text{-}n\text{-}C_4H_9)_2$ in C_4H_9OH and subsequent firing at temperatures up to 900 ° C.

It has been particularly difficult to prepare a homogeneous alkoxide solution, because copper alkoxides, $Cu(OR)_2$ (where $R \equiv$ Me, Et, Bu, etc.), are very sparingly soluble in common organic solvents such as alcohols, ethers and hydrocarbons. Hirano et al. [4] found that $Cu(OC_2H_4OC_2H_5)_2$ was a promising Cu source which could be dissolved in 2-methoxyethanol.

Amines, which are known to coordinate to metal ions in solution, have been effective for readily dissolving both copper alkoxide and yttrium alkoxide in an alcohol. Homogeneous alcoholic solutions of yttrium, barium, and copper alkoxides can be prepared using alkanolamines.

Nonaka et al. [5] and Monde and Sakka [6] have synthesized superconducting $Ba_2YCu_3O_{7-\delta}$ films on polycrystalline PSZ substrates by a dip-coating technique from alcoholic solutions with diethanolamine or triethanolamine. However, the addition of amines results in much readier formation of $BaCO_3$ during the pyrolysis of organometallic precursor films owing to the difficulty of adding water for the hydrolysis. A trace amount of $BaCO_3$ coexists with the $Ba_2YCu_3O_{7-\delta}$ phase in films heat-treated at 800 °C. Heating above 900 °C is required to decompose $BaCO_3$ completely, at which point a reaction of $Ba_2YCu_3O_{7-\delta}$ precursors with the ZrO_2 substrate takes place to form $BaZrO_3$. Such films exhibited a $T_{c,end}$ of ~ 60 K, i.e. much lower than that expected for superconductors synthesized by solid-state reactions.

In contrast to the highly oligomeric, insoluble copper alkoxides, 2,4-pentanedionatocopper(II) 2-methoxyethoxide, which can be synthesized by an alcoholic exchange reaction, is readily soluble in polar solvents (Payne et al. [7,8]). They prepared $Ba_2YCu_3O_{7-\delta}$ powders and thin films from a homogeneous 2-methoxyethanolic solution of $Y(OC_2H_4OCH_3)_3$, $Ba(OC_2H_4OCH_3)_2$ and $(C_5H_7O_2)_2Cu_2(\mu\text{-}OC_2H_4OCH_3)_2$. The result indicates that the use of mixed-ligand alkoxides enabled preparation of homogeneous alcoholic solutions of alkoxides without introducing amines. However, the chemical composition of the precipitates shifted unfavourably to the copper-poor side owing to a preferred reaction between barium and copper alkoxides in solution. Thus, an excess amount of copper alkoxide must be dissolved in the solution to achieve the required stoichiometry in the final precipitates. Powders heated to 950 °C in either air or oxygen were contaminated with $BaCO_3$ formed by the reaction of barium compounds with the decomposition products of organic groups, as indicated in the thermal analysis shown in Fig. 1. Powders formed the $Ba_2YCu_3O_{7-\delta}$ phase above 900 °C and tended to initiate a diamagnetic transition at 89 K. Thin films can be also prepared by spin-coating of the solution. Barium carbonate formation was suppressed in films by rapid heating, as shown in Fig. 2. The formation of $BaCO_3$ upon pyrolysis of organic precursors should be avoided in the preparation of homogeneous films. Hirano et al. [9,10] have discovered that it is possible to reduce or suppress the formation of $BaCO_3$ during pyrolysis and to carry out the low-temperature synthesis of the $Ba_2YCu_3O_{7-\delta}$ phase by utilizing an O_3/O_2 mixture. $Ba_2YCu_3O_{7-\delta}$ powders and thin films can be fabricated by the sol–gel method using metal alkoxides and acetylacetonate, as shown in Fig. 3. $Y(O\text{-}i\text{-}Pr)_3$ and Ba metal were used as starting materials. Cupric organometallic compounds are limited as starting materials owing to their low solubilities in common organic solvents, as mentioned

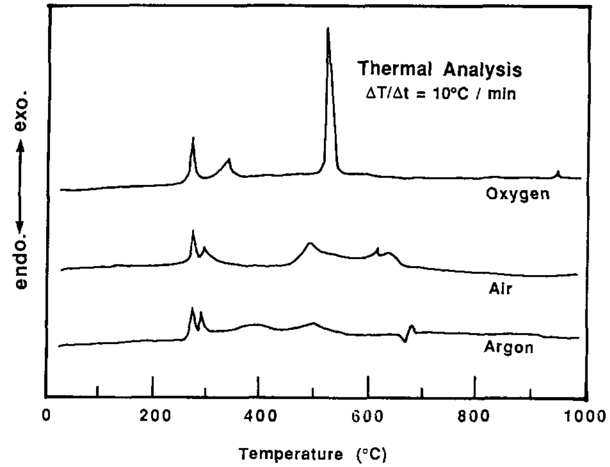

Fig. 1. DTA curves for powders prepared from unhydrolysed alkoxide solutions of Ba, Y and Cu with the composition 2 : 1 : 3 at a heating rate of 10 °C min^{-1} in argon, air, and oxygen (from W.G. Fahrenholtz et al. [7]).

above. $Cu(OC_2H_5)_2$, $Cu(OC_2H_4OC_2H_5)_2$, $Cu(acac)_2$, and $Cu(C_{17}H_{35}COO)_2$ of chemical reagent grade were examined as sources of Cu compounds. The solubilities of the Cu compounds in various organic solvents are summarized in Table 1. $Cu(OC_2H_5)_2$ is insoluble in common organic solvents except for amines and acetylacetone, which tend to form coordination compounds with Cu compounds readily. Copper stearate is soluble in toluene, pyridine and acetylacetone solvents, but these solvents are not suitable for $Y(O\text{-}i\text{-}C_3H_7)_3$ and $Ba(O\text{-}i\text{-}C_3H_7)_2$. $Cu(acac)_2$ is soluble in 2-methoxyethanol and 2-ethoxyethanol. $Cu(OC_2H_4OC_2H_5)_2$ is soluble in 2-ethoxyethanol, tetrahydrofuran (THF) and amine solvents. From this, $Cu(acac)_2$ and

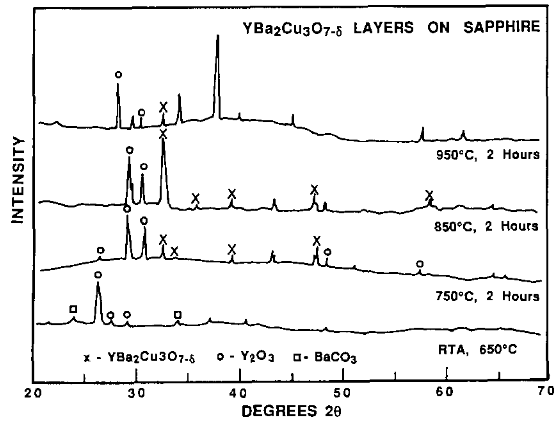

Fig. 2. X-ray diffraction data for $Ba_2YCu_3O_{7-\delta}$ thin layers prepared by rapid thermal processing (from W.G. Fahrenholtz et al. [8]).

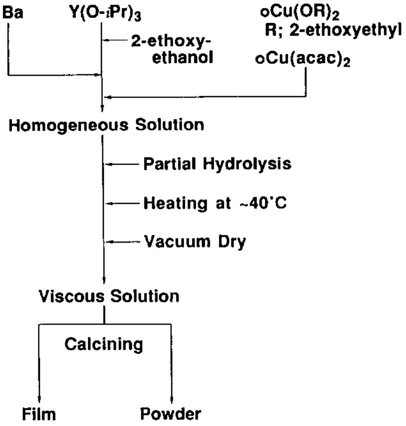

Fig. 3. Flow chart for chemical processing of $Ba_2YCu_3O_{7-\delta}$ through an organometallic route (from S. Hirano et al. [10]).

$Cu(OC_2H_4OC_2H_5)_2$ were selected as starting materials. 2-Methoxyethanol and 2-ethoxyethanol were found to be the most suitable of the common organic solvents for Ba, Y and Cu compounds. In this chemical processing,

TABLE 1

Solubility of cupric organometallic compounds [a]

Solvents	$Cu(Sta)_2$	$Cu(OEt)_2$	$Cu(OR)_2$ [b]	$Cu(acac)_2$
Hexane	–	x	–	–
Toluene	o	x	–	–
Triethylamine	–	x	–	–
Diethylamine	–	o	o	–
Diisopropylamine	–	x	–	–
Ethylene glycol dimethyl ether	x	–	x	x
Tetrahydrofuran	–	x	o	–
Pyridine	o	–	–	–
2-Methoxyethanol	x	–	x	o
1-Propanol	–	x	–	–
2-Propanol	x	x	–	x
Ethanol	–	x	–	x
Acetylacetone	o	o	–	x
2-Ethoxyethanol	–	–	o	o
Diethylene glycol	–	–	–	x
Methanol	–	–	x	–
2-Aminoethanol	–	o	–	–
Ethylene glycol	–	–	x	–
Hexamethyldisiloxane	x	–	–	–
Dimethyl sulfoxide	x	x	–	–
N,N-Dimethylformamide	x	x	–	–

[a] o, Soluble; x, insoluble or sparingly soluble.
[b] $R \equiv C_2H_4OC_2H_5$.

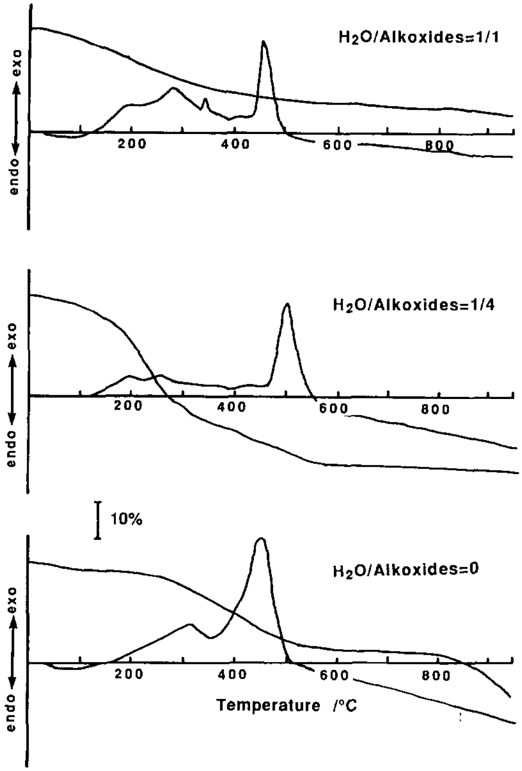

Fig. 4. DTA–TG curves of as-prepared specimens (by the hydrolysis of Y, Ba and Cu alkoxides at a heating rate of 10 °C min^{-1} in air) (from S. Hirano et al. [10]).

it is very important to control the hydrolysis and condensation processes in preparing a chemically homogeneous solution prior to the synthesis.

Figure 4 shows DTA–TG curves of as-prepared powders (using the hydrolysis of metal alkoxides). Two exothermic peaks and a gradual weight loss were observed for all powders at 200–300 °C and 400–500 °C in air, which correspond to the thermal decomposition and the oxidation of organic groups. In the as-prepared powders (using the partial hydrolysis of metal alkoxides), a less-noticeable weight loss was observed above 600 °C, while a large weight loss was observed above 800 °C for the specimens prepared without water addition (unhydrolysed), owing to the thermal decomposition of the $BaCO_3$ formed during pyrolysis.

In addition, when Cu(acac)$_2$ was used as a starting material instead of $Cu(OC_2H_4OC_2H_5)_2$, a more pronounced exothermic peak associated with a large weight loss was observed, suggesting some coordination between Cu(acac)$_2$ and 2-ethoxyethanol, and/or a partial exchange reaction of the acetylacetonate groups of the Cu compound with the solvent. Figure 5 indicates that chemically homogeneous powders of $Ba_2YCu_3O_{7-\delta}$ can be prepared only by the controlled partial hydrolysis of a homogeneous al-

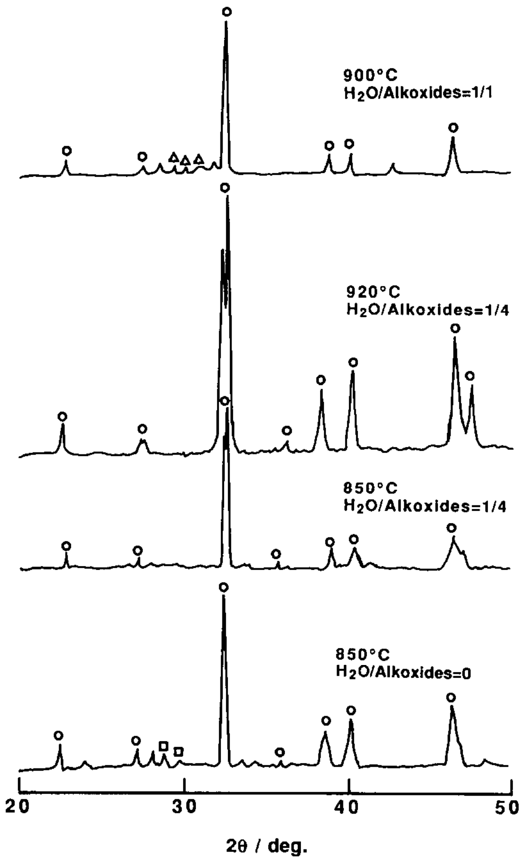

Fig. 5. X-ray diffraction patterns for $Ba_2YCu_3O_{7-\delta}$ powders calcined at 850 °C for 12 h, 900 °C for 7 h and 920 °C for 5 h (from S. Hirano et al. [10]). ○, $Ba_2YCu_3O_{7-\delta}$; △, Y_2BaCuO_5; □, $BaCuO_2$.

coholic solution of metal alkoxides with the addition of water less than the equivalent amount.

Furthermore, the crystallization of $Ba_2YCu_3O_{7-\delta}$ and the removal of the carbonate formed during pyrolysis were found to be accelerated effectively by heating the precursors in a flowing mixture of O_3/O_2 [9,10]. $Ba_2YCu_3O_{7-\delta}$ could be prepared as a single phase at a temperature as low as 750 °C. A reduction in the processing temperature might also eliminate problems related to the interaction commonly observed between $Ba_2YCu_3O_{7-\delta}$ and substrate materials [11]. The addition of O_3 results in direct formation of $Ba_2YCu_3O_{7-\delta}$ without the often-formed intermediate phases such as $BaCuO_2$ and Y_2BaCuO_5.

The importance of utilizing O_3 is in reducing or suppressing the formation of $BaCO_3$. For example, the carbon content in calcined powders at 850 °C in flowing pure O_2 was 2.24%, which was drastically decreased to 0.94% by

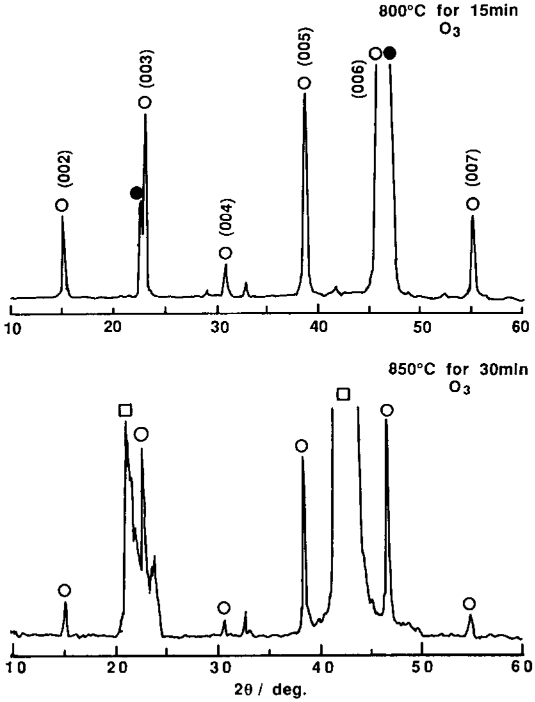

Fig. 6. X-ray diffraction patterns for $Ba_2YCu_3O_{7-\delta}$ thin films heat-treated at 800 °C for 15 min on the substrate $SrTiO_3(100)$ (top), and at 850 °C for 30 min on the substrate MgO(100) (bottom) in a flowing O_3/O_2 mixture (from S. Hirano et al. [12]). ○, $Ba_2YCu_3O_{7-\delta}$, ●, $SrTiO_3$; □, MgO.

using a mixture of O_3/O_2. $Ba_2YCu_3O_{7-\delta}$ ceramics thus fabricated at 920 °C from metal alkoxides became superconducting at about 83 K ($T_{c,end}$).

This chemical processing can also be applied in the synthesis of crystalline, stoichiometric $Ba_2YCu_3O_{7-\delta}$ thin films having a preferred orientation on single-crystal substrates by a dip-coating method [12]. It was found that $Ba_2YCu_3O_{7-\delta}$ began to form at temperatures as low as 650 °C as a result of the controlled partial hydrolysis of a homogeneous alkoxide solution and the use of an ozone/oxygen mixture. Single-phase $Ba_2YCu_3O_{7-\delta}$ thin films having the preferred orientation were directly synthesized on $SrTiO_3(100)$, $SrTiO_3(110)$ and MgO(100) substrates at 800 °C, as shown in Fig. 6. These thin films, prepared at 900 °C for 15 min, exhibited superconducting transitions at about 90 K ($T_{c,onset}$) and 75 K ($T_{c,end}$), as shown in Fig. 7.

Masuda and Tateishi [13] reported correlations of residual carbon in $Ba_2YCu_3O_{7-\delta}$ powders prepared using the sol–gel method with heating conditions (Fig. 8) and superconducting properties (Fig. 9). Carbon may remain, depending upon the firing conditions. X-ray photoelectron spectroscopy and Fourier-transform IR analyses showed that any residual carbon existed as carbonates and was concentrated at the surface of the powders.

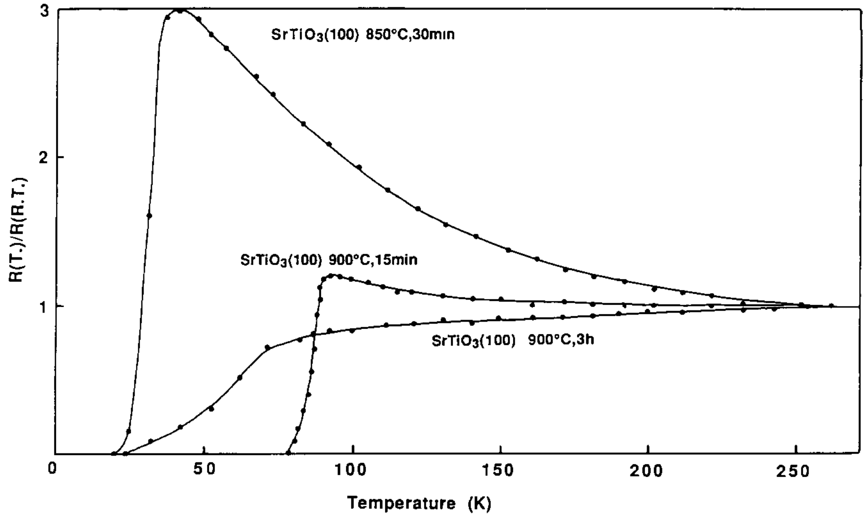

Fig. 7. Temperature dependence of d.c. resistivity of $Ba_2YCu_3O_{7-\delta}$ thin films prepared on the substrate $SrTiO_3$(100) (from S. Hirano et al. [12]).

Magnetic susceptibility and $T_{c,\text{onset}}$ of these powders were improved in proportion to the decrease in the carbonate content.

Horowitz et al. [14] have found, however, that it is possible to conduct the low-temperature synthesis of $Ba_2YCu_3O_{7-\delta}$ powders by decomposing carbon-free precursors in an inert gas. They used carbon-free precursors such as hyponitrites, which were precipitated from a nitrate solution by the addition of an aqueous solution of $Na_2N_2O_2$, and hydrated metal oxides,

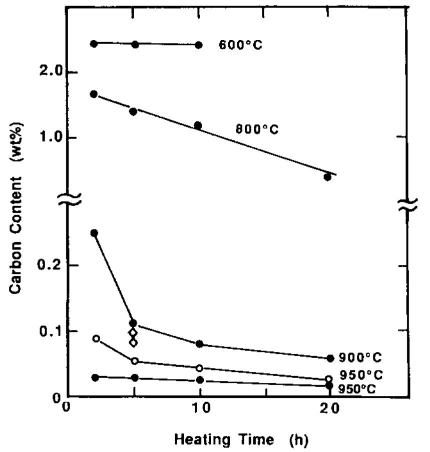

Fig. 8. Relation between heating conditions and carbon contents of $Ba_2YCu_3O_{7-\delta}$ calcined powders: ●, in O_2 flow; ○, in air flow. (From Y. Masuda et al. [13].) ◇ denotes powders obtained from a solid-state reaction.

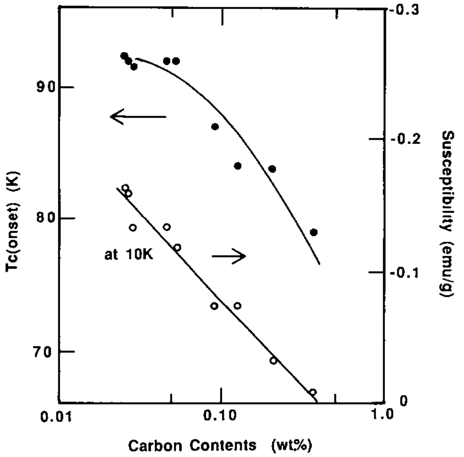

Fig. 9. Effect of carbon content on $T_{c,onset}$ and the magnetic susceptibility (at 10 K) of $Ba_2YCu_3O_{7-\delta}$ powders (from Y. Masuda et al. [13]).

which were prepared by the controlled hydrolysis of homogeneous THF solutions containing $Y(OCH(CH_3)_2)_3$, $Ba(OCH(CH_3)_2)_3$ and hydrolysable copper compound such as $Cu(OC(CH_3)_3)_2$, $Cu(N(C_4H_9)_2)$, or $Cu(OCH_2CH_2OC_4H_9)_2$. These precursors avoid the formation of $BaCO_3$ and lower the synthesis temperature. Conversion to the superconducting oxide was achieved by firing the precursors in flowing argon at 650–700 ° C for 2–12 h, yielding a tetragonal $Ba_2YCu_3O_{7-\delta}$ which was subsequently oxidized to the orthorhombic phase by annealing in flowing oxygen at 400 ° C for 2–12 h. Although $BaCO_3$ was not detected in the specimens, a trace of $BaCuO_2$ coexisted with the $Ba_2YCu_3O_{7-\delta}$. Further annealing at 950 ° C in oxygen resulted in a nearly pure $Ba_2YCu_3O_{7-\delta}$ phase. When the decomposition of the precursors is conducted in oxygen rather than argon, the $Ba_2YCu_3O_{7-\delta}$ phase does not form below 700 ° C. Manthiram and Goodenough [15] also recognized that annealing at relatively low temperatures in an inert atmosphere would yield a tetragonal phase suitable for subsequent oxidation to the superconducting orthorhombic form.

$Ba_2YCu_3O_{7-\delta}$ fibres can also be synthesized by the sol–gel method using organometallic compounds. Laine et al. [16] fabricated $Ba_2YCu_3O_{7-\delta}$ precursor fibres which were spun or extruded from a organometallic spinnable solution and then pyrolysed to form superconducting orthorhombic and tetragonal phases.

COPRECIPITATION METHODS

Three methods using coprecipitation reactions, i.e. of oxalate, carbonate and citrate, are discussed. The coprecipitation method permits the synthesis of superconducting oxide powders via a single calcination step without grinding. The main characteristics of the coprecipitation method are as follows: (1) a simultaneous and controlled precipitation of all the components with a given chemical composition; (2) a reproducible manufacturing process; and (3) potential for the synthesis of pure, homogeneous and fine-grained powders.

However, experimental conditions have to be carefully controlled in order to approach the above requirements. During the course of the fabrication process, all the components in the solution must precipitate simultaneously in a fixed composition with a precipitating agent. Furthermore, the pH of the solution has to be controlled to a given value in order to maximize the quantity of precipitate formed.

Oxalate coprecipitation

In the oxalate coprecipitation method, yttrium, barium, and copper nitrates are dissolved in water. Addition of an aqueous solution of oxalic acid immediately produces precipitation of the corresponding oxalates. However, the precipitation conditions, such as pH, concentration, temperature, and the relative ratios of metal ions, all have to be strictly optimized and controlled so that the solubilities of all three compounds of Ba, Y and Cu are simultaneously as low as possible. The three oxalates are almost insoluble in pure water, while barium oxalate does dissolve in acidic solutions. Therefore, the pH value must be controlled by means of a precipitating agent such as NaOH, NH_4OH. Even so, it is difficult to precipitate barium oxalate completely. The initial concentration ratios of the metal ions must be adjusted to achieve the proper stoichiometry in the final precipitate. So far, there have been no reports with detailed data concerning precise experimental conditions.

Caillaud et al. [17] have presented a theoretical model of the oxalate coprecipitation method which permits the most appropriate conditions to be chosen. Its application to the synthesis of $Ba_2YCu_3O_{7-\delta}$ has been experimentally examined. When preparing a solution with a pH between 2.38 and 2.53 and with yttrium, barium and copper concentrations at a level of 10^{-2} mol l^{-1}, the coprecipitation yield reaches 90%. The decomposition behaviour of the coprecipitates can be understood from a TG curve of single oxalates, as shown in Fig. 10. For yttrium oxalate the decomposition starts between 100 °C and 230 °C, resumes at 500 °C, and ends at about 700 °C. The entire decomposition of copper oxalate occurs between 230 °C and 260 °C. Barium oxalate transforms into $BaCO_3$ by heating up to 500 °C, which then starts to decompose into barium oxide at 800 °C

Oxalate coprecipitates were converted to a $Ba_2YCu_3O_{7-\delta}$ single phase by firing at 850 °C for 8 h in flowing oxygen. Although the oxalate decomposition caused the formation of $BaCO_3$, the temperature of conversion to

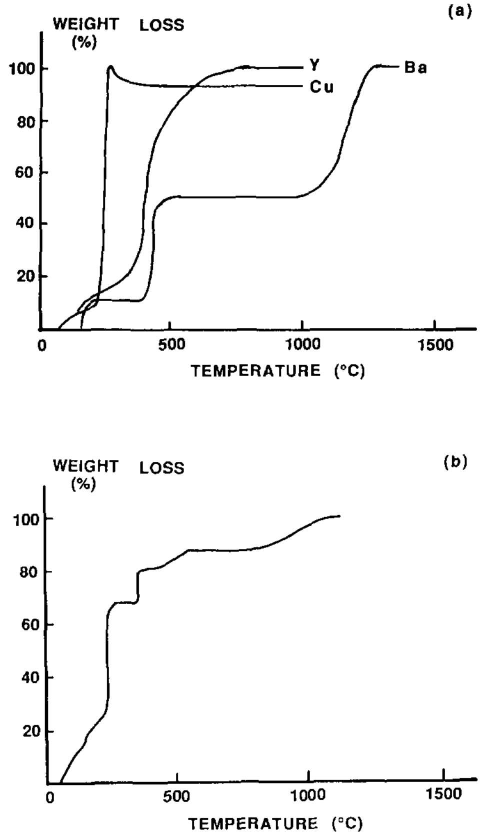

Fig. 10. TG curves of single oxalates (top) and the coprecipitate prepared at pH 2.46 (bottom). Heating rate, 4 °C min^{-1} (from F. Caillaud et al. [17]).

$Ba_2YCu_3O_{7-\delta}$ was still lower by about 100 °C than that in the solid-state reaction of mechanically mixed oxides. This may result from the high reactivity of coprecipitate-derived powders in a well mixed state.

Carbonate coprecipitation

Yttrium, barium, and copper carbonate powders are prepared by adding a metal nitrate solution to a sodium carbonate solution. NaOH was used to adjust the final pH of the mixed solution to a range of 9–10. In order to complete the precipitation reaction, a slight excess of Na_2CO_3 must be added to the original solution. To remove residual sodium ions in precipitates, carbonate powders must be rinsed with distilled water several times until the pH of the filtrate becomes $\leqslant 7.5$. Finally, the powders are dried in air at 80 °C. Carbonate precipitates were uniform in size, about 0.1–0.2 μm thick. $Ba_2YCu_3O_{7-\delta}$ ceramics sintered at 960 °C showed superconductivity at a $T_{c,end}$ value of 92 K.

Citrate coprecipitation

Amorphous citrates are also a useful intermediate for oxide superconducting materials. The typical procedure for preparing $Ba_2YCu_3O_{7-\delta}$ powders and films is shown in Fig. 11. This process is based on the ability of α-hydroxylic acids, such as citric acid, to form a polybasic acid chelate with metallic ions. The chelates undergo a polyesterification reaction when heated with a polyfunctional alcohol, such as ethylene glycol, forming a metal-containing polymer (not an organometallic compound). On further heating, a viscous resin, gel and, finally, fine oxide powders are produced.

This method therefore offers better compositional control and mixing at the molecular level in solutions compared with oxalate coprecipitation in which incomplete precipitation occurs occasionally owing to different solubilities of metal ions depending on the pH. It is possible to prepare powders and films by controlling the viscosity of the solution, which is determined primarily by the extent of polymerization.

Falter et al. [18] have synthesized superconducting $Ba_2YCu_3O_{7-\delta}$ powders by the citrate coprecipitation method. The phase development in this system is illustrated in Fig. 12. Amorphous precursors contained metallic copper formed during pyrolysis. After heating for 2 h at 575 °C, several crystalline phases were identified, namely $BaCO_3$ and CuO. These phases remained up to 750 °C and reacted at 800 °C to give the desired $Ba_2YCu_3O_{7-\delta}$ phase. In this system, crystallization from the amorphous precursor resulted in fine, well-mixed crystallites of Y_2O_3, $BaCO_3$ and CuO, which reacted to form the $Ba_2YCu_3O_{7-\delta}$ phase at 800 °C. Furcone et al. [19] fabricated $Ba_2YCu_3O_{7-\delta}$ thin films from homogeneous liquid citrate precursors by spin-coating and subsequent heat-treatment as follows: (1) pyrolysis at slow rates to 600 °C in

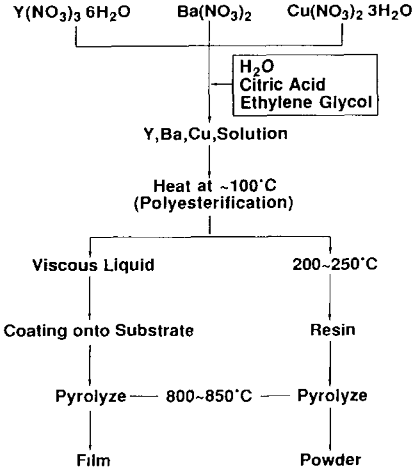

Fig. 11. Flow chart for a citrate coprecipitation process.

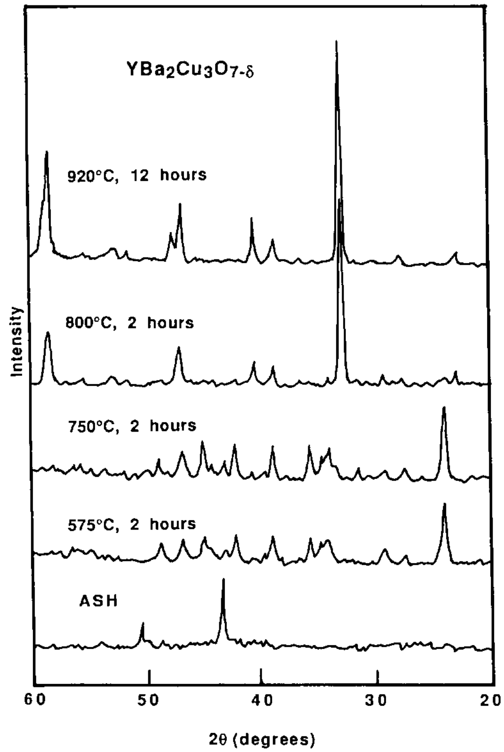

Fig. 12. X-ray diffraction patterns for $Ba_2YCu_3O_{7-\delta}$ powders after heat treatment (from L.M. Falter et al. [18]).

air; (2) vacuum firing to 800–850 °C; (3) annealing at 800–850 °C for 1–2 h; (4) cooling in oxygen to 400–450 °C and maintaining for 1–2 h.

X-ray diffraction analysis showed that the films were predominantly $Ba_2YCu_3O_{7-\delta}$, although some were contaminated with small amounts of Y_2BaCuO_2 and $BaCuO_2$. After vacuum firing for at least 2 h, no $BaCO_3$ was observed.

The onset of the superconducting transition is observed at 87 K with a $T_{c,end}$ value of 51 K. The transition temperature is lower than that expected for fully oxidized $Ba_2YCu_3O_{7-\delta}$. Critical current densities of $\sim 10^4$ A cm^{-2} are greater than those for most bulk ceramics, but lower by a factor of 10^2 than those of physically deposited expitaxial films. This is attributed to incomplete oxidation resulting from the presence of residual carbon, despite careful pyrolysis procedures with vacuum-firing.

CONCLUSIONS

The chemical synthesis of the superconducting oxides through solutions is a promising route to preparation of the desired powders, films or fibres having chemical homogeneity on a large scale. Extensive basic research still has to be carried out, especially on the critical selection of starting solutions and the fabrication procedures associated with polycondensation reactions for precursors. A clue may be drawn from the reports published so far: the key is to control the coordination of ions in the solution with metal-oxygen–metal bonds and to minimize the formation of carbonates during the pyrolysis of organometallic-derived precursors.

REFERENCES

1 E.C. Behrman, V.R.W. Amarakoon, S.R. Axelson, A. Bhargava, K.G. Brooks, V.L. Burdick, S.W. Carson, N.L. Corah, J.F. Cordaro, A.N. Cormack, D.G. DiCarlo, A. Dwivedi, G.S. Fischman, J. Friel, M.J. Hanagan, R.L. Hexemer, M. Heuberger, K.-S. Hong, J.-Y. Hsu, W.-D. Hsu, P.F. Johnson, W.C. LaCourse, J.R. LaGraff, M. Lakshminarasimha, J.W. Laughner, A.V. Longobardo, P.F. Malone, P.H. McCluskey, D.M. McPherson, T.J. Mroz, C.W. Rabidoux, J.S. Reed, P. Sainamthip, S.C. Sanchez, C.A. Sheckler, W.A. Schulze, V.K. Seth, J.E. Shelby, S.H.M. Shieh, J.J. Simmins, J.C. Simpson, R.L. Snyder, D. Swiler, J.A.T. Taylor, R. Udaykumar, A.K. Varshneya, S.M. Vitch and W.E. Votava, Adv. Ceram. Mater., 2 (1987) 539.

2 H.S. Horowitz, R.K. Bordia, C.C. Torardi, K.J. Morrissey, M.A. Subramanian, E.M. McCarron, J.B. Michel, T.R. Askew, R.B. Flippen, J.D. Bolt and U. Chowdhry, Solid State Ionics, 32/33 (1989) 1087.

3 S. Shibata, Takeshi Kitagawa, Hisaaki Okazaki, T. Kimura and T. Murakami, Jpn. J. Appl. Phys., 27 (1988) L53.

4 S. Hirano, T. Hayashi, R.H. Baney, M. Miura and H. Tomonaga, Chem. Lett., (1988) 665.

5 T. Nonaka, K. Kaneko, T. Hasegawa, K. Kishio, Y. Takahashi, K. Kobayashi, K. Kitazawa and K. Fueki, Jpn. J. Appl. Phys., 27 (1988) L867.

6 T. Monde and S. Sakka, Proc. MRS Int. Meet. on Advanced Materials, 6 (1989) 233.

7 W.G. Fahrenholtz, D.M. Millar and D.A. Payne, in M.F. Yan (ed.), Ceramic Superconductors II, American Ceramics Society, 1988, p. 141.

8 W.G. Fahrenholtz, D.M. Millar and D.A. Payne, Proc. Symp. on Ceramic Superconductors, 23–27 April, 1989, Indianapolis, in press.

9 S. Hirano, Jpn Patent, Application 63-6560 (1988), Kokai-183479 (1989).

10 S. Hirano, T. Hayashi, M. Miura and H. Tomonaga, Bull. Chem. Soc. Jpn., 62 (1989) 888.

11 C.T. Cheung and E. Ruckenstein, J. Mater. Res., 4 (1989) 1.

12 S. Hirano, T. Hayashi and M. Miura, J. Am. Ceram. Soc., 1990, in press.

13 Y. Masuda and T. Tateishi, J. Jpn. Soc. Powder and Powder Metal., 36 (1989) 501.

14 H.S. Horowitz, S.J. Mclain, A.W. Sleight, J.D. Druliner, P.L. Gai, M.J. Vankavelaar, J.L. Wagner, B.D. Biggs and S.J. Poon, Science, 243 (1989) 66.

15 A. Manthiram and J.B. Goodenough, Nature, 329 (1987) 701.

16 R.M. Laine, K.A. Youngdahl, W.M. Carty, G.C. Stangle, C. Han, R.A. Kennish, S. McElhaney, T.K. Yin, T. Yogo, M. Sarikaya, in M.F. Yan (Ed.), Ceramic Superconductors II, American Ceramics Society, 1988, p. 450.

17 F. Caillaud, J.F. Baumard and A. Smith, Mater. Res. Bull., 23 (1988) 1273.

18 L.M. Falter, D.A. Payne, T.A. Friedmann, W.H. Wright and D.M. Ginsberg, personal communication.

19 S.L. Furcone, Y.M. Chiang, J.A.S. Ikeda and D.A. Rudam, in M.F. Yan (ed.), Ceramic Superconductors II, American Ceramics Society, 1988, p. 490.