

FEATURE ARTICLE

Chemical Routes for Preparation of Oxide High-temperature Superconducting Powders and Precursors for Superconductive Ceramics, Coatings and Composites

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The importance of chemical routes for the preparation of high-temperature superconducting (HTSC) powders is discussed as well as preparative peculiarities of their synthesis by coprecipitation, sol-gel, freeze-drying and spray pyrolysis techniques.

The discovery of ceramic high-temperature superconductors has spurred enormous scientific and practical interest to elucidate the nature of the phenomenon¹ as well as to find its practical application.^{2,3} Very soon it became evident that success in both of these is determined by the techniques used to obtain HTSC materials and, first of all, of powders as precursors for HTSC ceramics, coatings and composites.

At first the so-called 'ceramic technique' was used. This involved intimate mechanical mixing of the oxides (for the 123 phase: yttrium and copper oxides with barium carbonate) and repeated 'beat and heat' cycles to achieve complete solid-phase interaction of the reagents. In some cases the oxides were replaced by the more readily available carbonates, nitrates or other salts.

This technique was well established by its use for obtaining all kinds of constructional and functional ceramics, but it has considerable disadvantages. The greatest disadvantage is the highly crystalline (10 μm) nature of the reagents and the need to achieve heterogeneous mixing, necessitating multiple repetitions of prolonged thermal treatment and grinding. In this case uncontrolled crystallite growth takes place and, as a consequence, results in chemical and granulometric heterogeneity of anisotropic HTSC grains, leading to irreproducibility of electrical and magnetic properties.

Between 1987 and the present time many investigations into HTSC technologies have been connected with the development and application of so-called 'chemical techniques' for the preparation of powders.^{4,5} Chemical techniques increase the homogeneity of the product by mixing the reagents at the molecular level in solution and maintaining this level (more or less successfully) during the following synthetic stages. The oxide powders prepared in this way have high specific surface area and, consequently, readily undergo solid-state interaction and sintering.⁶

In Fig. 1 the efficiency of chemical techniques of synthesis for increasing the homogeneity of ceramics is illustrated using values of the standard deviation in an analysis of the composition of Y- and Bi-containing ceramics using sputtered neutral mass spectrometry (SNMS).⁷ Low standard deviations imply greater reproducibility of layer-by-layer analysis of bulk samples. In turn the reproducibility is governed by the chemical homogeneity. From the figure it can be seen that chemical routes are preferable.

The use of chemical techniques for the preparation of powders may be useful even for the most popular melting techniques that are used to obtain HTSC powders, notwithstanding the considerable smoothing of the morphological differences of powders with different backgrounds due to

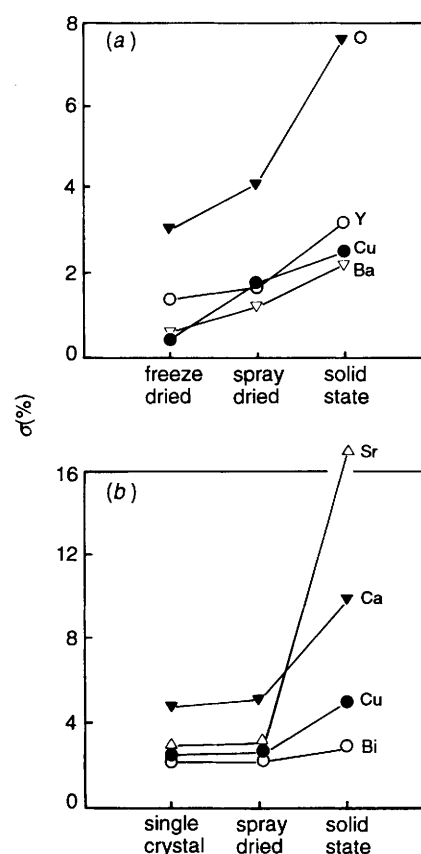


Fig. 1 Reproducibility (standard deviation, σ) of SNMS data for (a) YBa₂Cu₃O_{7-x} and (b) Bi₂Sr₂CaCu₂O_{8-x} ceramics

complete or partial melting. In particular, in order to elucidate the nature and influence of various pinning centres on superconducting properties a considerable role must be played by purity or the controlled content (size and distribution) of impurities, and this can be ensured most easily by chemical techniques of synthesis.

We shall examine the following techniques: (1) coprecipitation techniques, (2) sol-gel processes, (3) spray drying, (4) plasmochemical techniques and (5) cryochemical techniques.

The aim of the present examination is to explain the potential of the different techniques and to highlight specific features of their use in the preparation of HTSC powders.

At present some families of oxide HTSC phases are known, including La_{2-x}M_xCuO₄ (M = Ba, Sr), Y₂Ba₄Cu_{6+n}O_{14+n} ($n =$

	I	II	III	IV	V
	K	Ca	Sc	Ti	V
4	Cu	Zn	Ga	Ge	As
	Rb	Sr	Y	Zr	Nb
5	Ag	Cd	In	Sn	Sb
	Cs	Ba	La	Hf	Ta
6	Au	Hg	Tl	Pb	Bi

Fig. 2 Portion of Periodic Table emphasizing the position of HTSC-forming elements

0–2), $\text{RE}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n}$ ($n=0-2$), $\text{Bi}_2(\text{Ca},\text{Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4}$ ($n=1-3$), $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ or $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ ($n=1-3$), $\text{PbSr}_2\text{ACu}_2\text{O}_6$ or $\text{Pb}_2\text{Sr}_2\text{ACu}_3\text{O}_8$ ($A=\text{Y, RE, RE}+\text{Sr, RE}+\text{Ca}$), $\text{RE}_{2-x}\text{Ce}_x\text{CuO}_4$, $\text{Sr}_{1-x}\text{M}_x\text{CuO}_2$ ($M=\text{Sr, RE}$) and $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$. They are all complex oxides and include oxides of copper, alkaline-earth elements and oxides of yttrium, rare-earth elements, bismuth, thallium, lead or mercury. Differences in properties of components of HTSC phases conditioned by their position in the Periodic Table (Fig. 2) makes it impossible to produce a unified synthesis pattern even for a single synthetic technique. At the same time, the presence of such components as copper or alkaline-earth metals in all HTSC phases allows a prognosis to be made regarding the applicability of different techniques. It is evident that coprecipitation using ammonia can disturb copper stoichiometry, and coprecipitation in the form of carbon-containing salts is always accompanied by the formation of alkaline-earth-metal carbonates and by prolonged times of thermal treatment. Losses of some components of the HTSC phases (thallium, mercury, lead) due to their high volatility can be decreased by treating a complex oxide precursor synthesized by one of chemical techniques in a vapour of the volatile component. This technique was developed for thallium systems⁸ and was shown to be highly efficient for the synthesis of mercury-containing HTSC⁹ materials.

In this review most attention will be paid to the synthesis of Y- and Bi-containing phases as these are the most commonly used and investigated phases. Note that the attribution of a synthesis technique to one of above-cited classes is purely nominal (especially in case of coprecipitation and sol-gel techniques) and is determined by the author's point of view. Also, we shall consciously limit consideration of powders as precursors because many properties of HTSC ceramics are determined not only by the method of preparing the powders, but also by the conditions of posterior thermal treatment, which are frequently not optimal for a given powder prehistory.

Chemical Coprecipitation Techniques

Coprecipitation techniques have a wide application in the synthesis of various kinds of ceramics. Therefore it is not surprising that they were among the first chemical techniques to be used to prepare HTSC powders. By using the correct

experimental technique in some cases it is possible to obtain reproducible homogeneous disperse salt mixtures with the desired ratio of cations. In the ideal case (which is not achieved because of the different chemical nature of the components) the optimal conditions are where the precipitation of cations from solution occurs simultaneously and with the same rate. The most common salts for obtaining HTSC precursors are oxalates and carbonates.

Coprecipitation of Oxalates

To precipitate oxalates the nitrates^{10,11} or acetates^{12,13} are used as one initial reagent and then mixtures of oxalic acid–ammonia, oxalic acid–triethylamine^{14–17} or a saturated solution of ammonium oxalate, with fixed solution acidity (pH), or an aqueous solution of dimethyl oxalate¹² are used as precipitants. The precipitation process is complicated by the very different dependence of solubility on pH of yttrium, barium and copper oxalates and the concentrations of initial reagents.^{10,18,19}

Individual oxalates of yttrium and barium are precipitated completely by $\text{pH} > 2.5$ [Fig. 3(a)] and their solubility depends on the initial concentration of nitrate; for yttrium oxalate, e.g., the solubility is at a minimum at $10^{-2} \text{ mol l}^{-1}$ [Fig. 3(b)]. Under the same conditions only 60% pure copper oxalate precipitates, but by simultaneous precipitation with yttrium and barium oxalates in the pH limit $2.38 < \text{pH} < 2.53$ it is possible to precipitate up to 90% of the cations from solutions

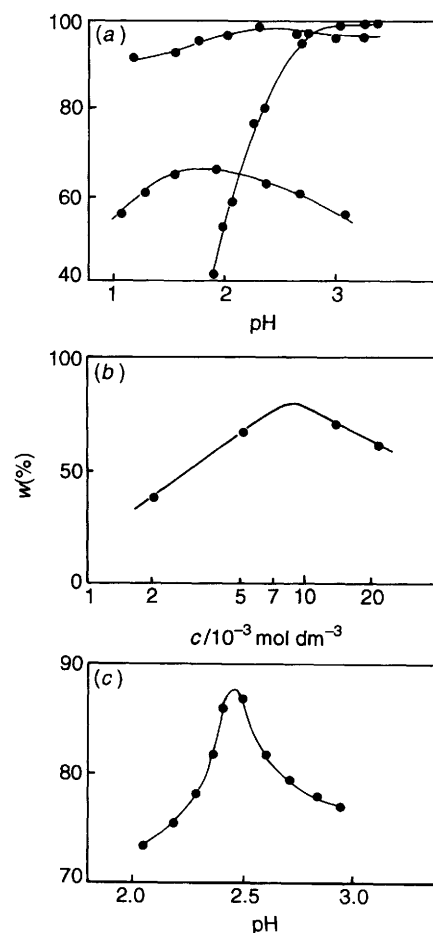


Fig. 3 Coprecipitation yield (w) of Y, Ba and Cu oxalates from individual [(a), (b)] and ternary (c) solutions as a function of pH [(a), (c)] and initial concentration of yttrium (b).¹⁰

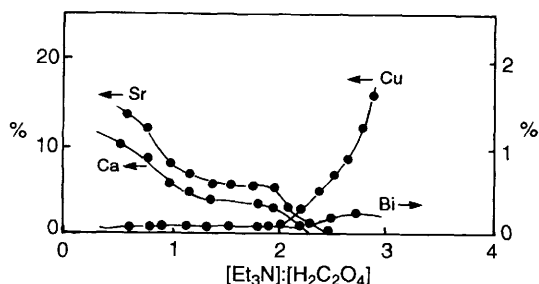


Fig. 4 Dependence of metal ion residuals in the filtrate on the triethylamine:oxalic acid ratio¹⁷

with concentrations $[Y] = 10^{-2} \text{ mol l}^{-1}$, $[Ba] = 2 \times 10^{-2} \text{ mol l}^{-1}$, $[Cu] = 3 \times 10^{-2} \text{ mol l}^{-1}$ [Fig. 3(c)].

A detailed analysis of the factors that affect complete precipitation of oxalates in the synthesis of Bi-containing HTSC in ref. 15 (for a phase with Bi: Sr: Ca: Cu = 1: 1: 1: 2) yielded the following recommendation: a mixture of 1 mol l⁻¹ solutions of strontium, calcium and copper nitrates (14, 10 and 20 ml, respectively) and 10 ml of a 1 mol l⁻¹ solution of bismuth nitrate must be added simultaneously with strong stirring to 102 ml of 0.5 mol l⁻¹ solution of oxalic acid. The suspension obtained must be diluted to 900 ml with water and added to 110 ml of 1 mol l⁻¹ NaOH (pH 5). The precipitate formed must be filtered off, washed with water and then washed three times with acetone and dried at 80 °C (12 h). The oxalate mixture obtained has a specific surface area (up to 90 m² g⁻¹) and consists of agglomerates (1–10 µm, average size 3.8 µm) of fine (0.25 µm) particles.

Coprecipitation of oxalates with a triethylamine–oxalic acid mixture has been used for the preparation of precursors in Y^{14,16} and Bi¹⁷ systems. Precipitation is achieved by adding (dropwise) a mixture of nitrate solutions to the cooled (0 °C) precipitant solution. The dependence of the cation concentration after precipitation on the molar ratio of triethylamine to oxalic acid is shown in Fig. 4. It is evident that complete precipitation is possible only for a ratio of 2.2: by using lower values the precipitate is depleted in calcium and strontium and by using higher ratios the precipitate is depleted in copper and, partially, in bismuth.

Using an aqueous solution of dimethyl oxalate¹² as precipitant from acidic (pH 0.9) solution it was possible (by continuous stirring for a week) to precipitate completely a precursor for the synthesis of the 2223 Bi phase. Quantitative precipitation of oxalates is also achieved by adding excess (three times) of boiling ethanolic solution of oxalic acid to a hot solution of the corresponding nitrates.²⁰

Oxalate powders obtained after filtration and drying are characterized by particles of size 0.3–0.5 µm and specific surface area up to 40 m² g⁻¹. Heating the coprecipitated oxalates (dried at 20 °C) at 6 K min⁻¹ causes the following processes to occur:¹¹ 65 °C, two-stage dehydration of barium oxalate; 200 °C, decomposition of copper oxalate to oxide; 230 °C, decomposition of barium oxalate to carbonate; 355 °C, decomposition of yttrium oxalate to carbonate; 495 °C, decomposition of yttrium carbonate to oxide.

Complete decomposition of barium carbonate occurs when the precipitate is heated to 950 °C. As expected, the thermal decomposition of oxalates occurs before the formation of carbonates. From this point of view the process of coprecipitation has few advantages over the ceramic technique, but the high degree of homogeneity achieved by coprecipitation and the absence of melting by thermal treatment allow the formation of a single-phase product to be achieved more rapidly.

Coprecipitation of Carbonates

In principle, coprecipitation of carbonates is analogous to that of oxalates, the difference being that in oxalate precipitation the main attention is paid to complete precipitation of copper, whereas for carbonates the most soluble component is the barium salt. In the coprecipitation of carbonate HTSC precursors an excess of ammonium hydrogen carbonate,²¹ sodium carbonate²² or trimethylammonium carbonate²³ are used as precipitants. Coprecipitation is achieved at pH > 8 by the addition of ammonia or sodium hydroxide solution. In the latter case, as well as by precipitation with sodium carbonate, the precipitate must be washed carefully because alkali-metal impurities impair the properties of HTSC materials (this process may be accompanied by selective dissolution and deviation from stoichiometry).

Note that precipitated cations are present in precipitate not only as carbonates, but also as hydroxides. The filtered and dried carbonate–hydroxide mixture consists of 1–3 µm agglomerates of very fine (< 50 nm) particles, and the precursors obtained after thermal decomposition have a grain size of ca. 0.3 µm.²³ Decomposition of barium carbonate by heating the hydroxide–carbonate mixture begins at 600 °C and a single Y-123-phase is formed after the mixture is annealed at 935 °C for 24 h.

Untraditional Coprecipitation Techniques

In addition to the techniques of coprecipitation for obtaining HTSC precursors mentioned above some other techniques were of limited usefulness: coprecipitation of hydroxides from acetate solutions with organic amines,²⁴ coprecipitation of hydroxides with alkalis,²⁵ coprecipitation of tartrates with tartaric acid²⁶ and coprecipitation of carbonaceous precursors from nitrate solutions by addition of aqueous sodium hyponitrite, Na₂N₂O₂.²⁷

Sol–Gel Techniques

Citrate Technique

The variation of the sol–gel technique detailed below was proposed in 1967,²⁸ but it has gained acceptance only for the synthesis of HTSC powders.

The technique is based on the ability of hydroxyacids (citric acid, for example) to chelate metal ions. Heat treatment (100–140 °C) of the chelates with polyfunctional alcohols (e.g. ethylene glycol) yields oligomers by esterification. Further heat treatment (180–200 °C) causes further polymerization and a viscous resin (gel) is formed, the decomposition of which yields an oxide powder (Fig. 5). Supposing that complexes of citric acid and metal ions are homogeneously distributed in solution and this distribution is conserved after polymerization, the homogeneity should not be altered by decomposition. Therefore sol–gel techniques are recommended for work directed at the elucidation of the influence of impurities and/or substitutions on the properties of HTSC materials.

Apart from these considerations, the technique is not expensive because it requires no apparatus (absence of centrifugation, filtration, washing and drying operations), and nitrates are most frequently used as the initial reagents. The possibility of controlling the viscosity of the sol obtained (by varying the ratio of components, the time and temperature of polymerisation, Fig. 6) allows the technique to be considered for preparation not only of powder, but also of thick films, fibres and flat ceramic forms.²⁹ The powders obtained possess a high activity, which allows lower temperatures and processing times to be used for synthesis and sintering.

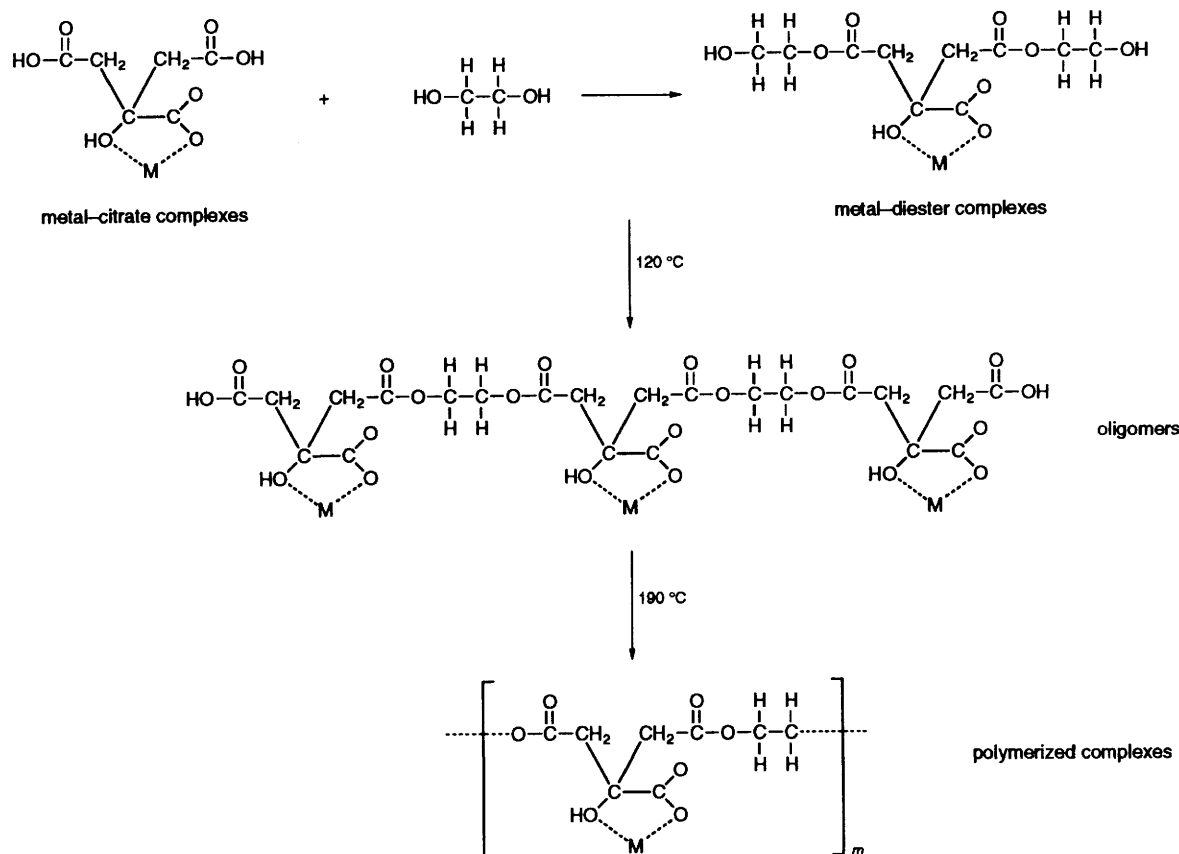


Fig. 5 Scheme of the chemical processes involved in the citrate sol-gel synthesis of ceramics

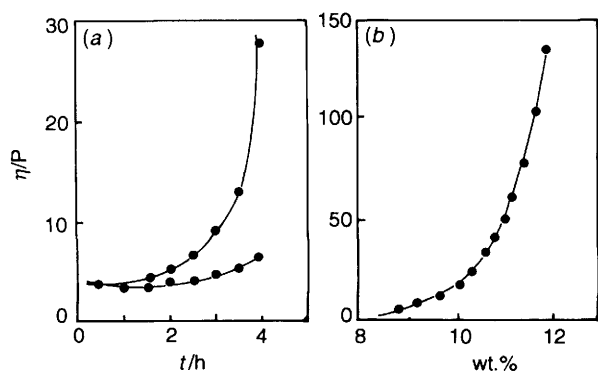


Fig. 6 Viscosity of citric acid-ethylene glycol (1:4) solution as function of heating time (a) and of weight concentration of salts (for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ synthesis) (b)²⁹

The sol-gel process is carried out as follows. To a mixture of aqueous nitrates and ethylene glycol (to which ammonia is sometimes added to increase the pH to 3–5³⁰) a solution of citric acid is added in ratio of 1 equivalent of acid to 1 equivalent of metal. Commonly ethylene glycol is in excess because hydroxy groups stabilize metal-citrate complexes in solution and favour the formation of oligomers.

A specific problem encountered in the synthesis of Bi-containing HTSC is the stabilization of bismuth cations in soluble form. It is known that Bi^{3+} cations are readily hydrolysed in aqueous media to form insoluble oxynitrates. To keep bismuth in soluble form it is necessary to add an excess of nitric acid, which in turn suppresses the dissociation of citric acid and disrupts the formation of stable metal-citrate complexes. This problem was resolved for the sol-gel technique in the following way.³¹ Solutions of bismuth nitrate

in ethylene glycol and aqueous citric acid were mixed in the ratio of 3.96 g of citric acid to 10 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (+ 50% excess of ethylene glycol to the water required for dissolution of citric acid). The excess of ethylene glycol, which has two hydroxy groups with strong complexing activity, stabilizes the bismuth cations: despite the low acidity a precipitate does not form. The solution obtained is then mixed with a solution of nitrates of lead, strontium, calcium and copper in an ethylene glycol-citric acid mixture.

Dehydration and concentration are achieved by prolonged heating (several hours) at temperatures not exceeding 140°C . The process is accompanied by segregation due to redox processes in the system. Note that the colloidal solution formed after evolution of NO_x is unstable, as shown by local evolutions of NO_x , the number of which is dependent on the temperature and time of aging.³²

Heating the mixture at *ca.* 190°C causes polymerization to occur accompanied by an increase in the viscosity and a change in colour from blue-green to brown-black. The size of the colloidal particles in the gel does not exceed 10 nm according to electronic microscopic data.³³ After the mixture is cooled a light-brown mass is obtained, which is transformed by grinding and heating into a mixture of oxides.

The activity that the oxide powders obtain after decomposition has been proved³³ by synthesis of single-phase Y-123 immediately after annealing at 800°C (5 h), *i.e.* considerably lower than the temperatures used in ceramic synthesis, and in ref. 34 where the Y-124 phase was obtained after sintering the sample at 815°C (120 h).

Kakihana *et al.*³⁵ compared the homogeneity of Y-123 ceramics prepared by the sol-gel and ceramic routes by X-ray and Raman spectroscopy. The ceramics were prepared by sintering pressed powders at 940°C (15 h), cooling to 400°C , annealing at this temperature (22 h) and further cooling in a

furnace. The ceramics were single phase (X-ray). That the ceramic produced by the sol-gel method was more homogeneous was proved by the absence of the characteristic bands of BaCuO_2 (580 and 640 cm^{-1}) and Y_2BaCuO_5 (390 and 605 cm^{-1}) in the Raman spectra. Comparison with standards showed that the impurity content did not exceed $0.5\text{ mass } \%$. Moreover the authors note that the size of grains is regular ($3\text{ }\mu\text{m}$) in ceramics prepared by the sol-gel route. Conversely the grains produced by the ceramic route were not homogeneous in size and there was evidence (in photomicrographs) that local melting had occurred during sintering, probably due to the initial chemical heterogeneity of the powder.

The sol-gel technique was successfully used for synthesis of precursors for lead-family HTSC.³⁶

Hydrolysis of Metal Alkoxides

An alternative technique, frequently classed among 'sol-gel' processes, is the so-called alkoxide technology. It is based on the preparation of powders (or thin films) by slow hydrolysis of a mixture of solutions of metal alkoxides. The method is suitable for the preparation of small quantities of extremely pure and homogeneous powders, as well as fibres, films and ceramics.³⁷ A disadvantage of the technique is the inaccessibility and expense of the initial reagents. In addition, a specific problem for HTSC production is the difficulty of preparing homogeneous mixtures of alkoxides because there are no readily available copper alkoxides that are soluble in common solvents. A method for increasing the solubility of copper in alcoholic solution has been proposed^{38,39} and involves boiling the copper alkoxide in an alcoholic solution of dimethylaminoethoxide. The compound formed $\{\text{Cu}[\text{OC}_2\text{H}_4\text{N}(\text{CH}_3)_2]_2\}$ is readily soluble in isopropyl alcohol (up to 10.5% of metal by weight).

Hydrolysis of the mixture of alkoxides is carried out at reflux by slow addition of aqueous alcohol (25%). After the solvent has been distilled off at low pressure an amorphous product is obtained, the thermal decomposition of which at 700°C gives a fine (*ca.* hundreds of Å) mixture of yttrium and copper oxides and barium carbonate. Formation of the Y-123 phase was observed at 800°C and a single-phase product was formed at 850°C (air, 3 h). Despite the fact that the alkoxide technique has no advantage from the point of view of temperature lowering and decreasing the time of synthesis, it may be useful for the preparation of coatings by the sedimentation technique.

Thermal Decomposition of Solutions

Pyrolysis of Aerosols

None of the chemical techniques for obtaining HTSC powders has such wide application as the pyrolysis of aerosols. This is a widespread technique for the preparation of fine disperse active powders for the production of HTSC materials. The essence of the technique consists of the following: using an ultrasonic pulveriser a mixture of salt solutions is transformed into an aerosol with a particle size of $0.5\text{--}0.8\text{ }\mu\text{m}$ and then carried by a flow of carrier gas to a hot chamber where instant (complete or partial) decomposition of the particles takes place. The oxide product is collected on a filter.

Mixing the components at the atomic level in solution and the practically instant dehydration and decomposition of microdrops of the aerosol allow a homogeneous product to be obtained avoiding the multiple grinding and annealing that characterise the ceramic technique and make the product impure and lead to uncontrolled growth of the grains. Nevertheless, the powders obtained may be contaminated by

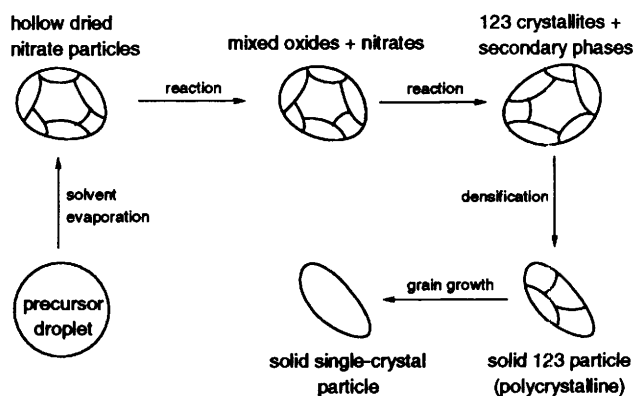


Fig. 7 Mechanism for formation of solid reacted particles from aerosol droplets⁴⁰

material from the pulverising chamber (high temperature, presence of free acid); in addition, to avoid formation of barium carbonate, it is necessary to purify large volumes of carrier gas (oxygen) from impurities (CO_2).

The parameters that determine the quality and properties of the powders are, first, the concentration of the solution, the temperature of the reactor and the time the particles spend in the hot zone of the reactor. This time is determined by the aerodynamic conditions of the reactor (geometry, gas rate).^{40–42} For example, relatively low temperatures ($700\text{--}800^\circ\text{C}$) and short heating times lead to the formation of porous particles ($25\text{--}50\text{ nm}$) and agglomerates of such particles that make their condensation difficult by following sintering, whereas at 1000°C and times of *ca.* 15 s it is possible to obtain monocrystalline (not agglomerated, $100\text{--}250\text{ nm}$) and practically single-phase particles (Fig. 7).⁴⁰ By using solutions of concentration 0.03 mol l^{-1} the ceramic obtained has an average grain size of $0.75\text{ }\mu\text{m}$ and from solutions of concentration 0.45 mol l^{-1} (with the same thermal history) average grains sizes of $2\text{ }\mu\text{m}$ are obtained.⁴²

The most widely used salts for this technique are nitrates. Their use allows the Y-124 phase to be obtained by annealing at 750°C for 24 h ($p_{\text{O}_2} = 1\text{ atm}$)⁴⁰ and a high content of the Bi-2223 phase to be obtained even after 16 h of annealing at 750°C .⁴¹ The Y-123 phase was successfully prepared by the pyrolysis of aerosols of citrate complexes with ethylene glycol,⁴³ formates,⁴⁴ glycinate (alanide)–nitrate⁴⁵ and acetate–nitrate⁴⁶ mixtures. In the last case, by the use of an optimal component ratio (oxidant:reducer) it is possible to perform the decomposition in one step (a peculiar version of self-propagation synthesis) at a substantially lower temperature (Fig. 8).

Plasmochemical Technology

Plasmochemical technology of preparation of powder precursors for HTSC ceramics is, in general, analogous to that of pyrolysis of aerosols. The technique is based on the introduction of an initial solution (concentration up to 40 g l^{-1}) by excessive pressure into a flow of low-temperature plasma formed by several plasmotrons (the output of a single plasmotron can achieve tens of kW).⁴⁷ There the dispersed solution decomposes into solid (powder) and gaseous (water vapour, nitrogen and oxides of carbon) phases, which are captured and absorbed by corresponding filters.

Argon or air are commonly used as the gas-forming plasma. The powders prepared have a size of $1\text{--}3\text{ }\mu\text{m}$ and specific surface areas of $5\text{ m}^2\text{ g}^{-1}$ and they are a mixture of copper and yttrium oxides and barium nitrate. In addition to the disadvantages of the aerosol pyrolysis technique, plasmochem-

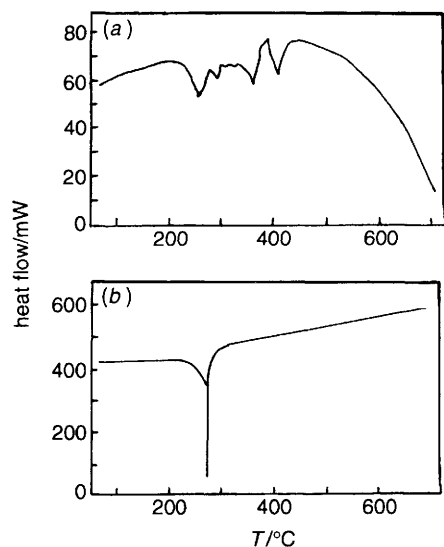


Fig. 8 DSC curves for the decomposition of all acetate precursors of the Y-123 phase (a) and the acetate–nitrate (6:7) mixture (b)⁴⁵

ical technology requires a great expense of energy and of carrier gas (tens of litres per min) and does not compensate for this in terms of product quality.

Cryochemical Technology

The disadvantages inherent in the majority of chemical techniques for the synthesis of HTSC powders (in both Y and Bi systems) can be eliminated by using cryochemical technology (spray-freezing/freeze-drying).⁴⁸ These are based on preparation of a finely dispersed and highly homogeneous salt (and then oxide) precursor using fast freezing of a finely dispersed solution of salts (obtaining a cryogranulate) and subsequent sublimation of water. It is necessary to carry out the experiment under conditions which avoid physicochemical processes leading to disturbance of the chemical and granulometric homogeneity of product. Such processes include: (1) stratification of dispersed microdrops into regions rich and poor in solvent due to insufficiently high cooling rates [this can be avoided if the solution is dispersed not into liquid nitrogen (or in cooled hexane) but onto a massive metal plate cooled to liquid-nitrogen temperature]. (2) Melting of the cryogranulate in the course of freeze-drying due to formation of low-melting eutectics (in the case of nitrate solutions there is a eutectic of H_2O – HNO_3 with $T_m = -43^\circ\text{C}$). To remove this problem it is necessary to try to exchange nitrate solutions for acetates⁴⁹ (but in this case the problem of formation of carbonates and their decomposition arises), or for nitrate–nitrite solutions,⁵⁰ or to use dilute solutions of nitrates with low acidity (0.1 mol l^{-1} Bi at pH 0.7) by synthesis of the Bi(Pb)-2223 phase.⁵¹ (3) Segregation of components in the freeze-dried product (containing up to 3 mass % of water) during its thermal treatment due to the melting of hydrates, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (42°C) and $\text{Cu}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (112°C). In this case the drying must be carried out in a thin layer at slow (5 K h^{-1}) heating to 125°C in an argon flow.⁵¹ (4) Undesirable formation of carbonates during annealing due to the presence of CO_2 in the atmosphere. It is not sufficient in this case to use air that is cleansed of carbon dioxide; it is more efficient to achieve the necessary partial pressure of oxygen by mixing oxygen and argon in the required ratio. (5) The occurrence of solid-state interactions under conditions that exclude the formation of liquid phases. This is especially vital in the synthesis of Bi-containing HTSC because the

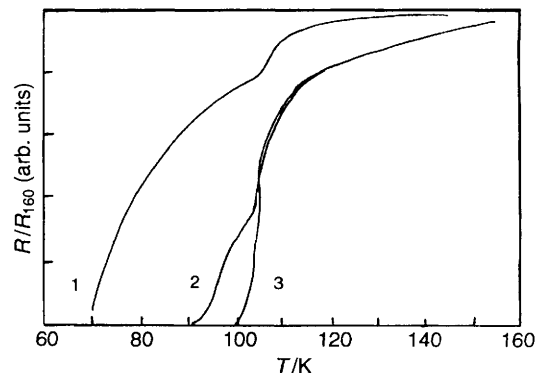


Fig. 9 Temperature dependence of the normalized resistivity for the Bi(Pb)-2223 phase ceramics with different prehistory: 1, solid state; 2, sol–gel; 3, freeze-drying⁵⁴

temperature of formation of liquid phases in the process depends very strongly on partial pressure of oxygen (836°C at $p_{\text{O}_2} = 1 \text{ atm}$, 808°C at 0.2 atm , 772°C at $2 \times 10^{-2} \text{ atm}$). In addition, it is recommended^{50,51} that the salt product is introduced into a furnace that has been pre-heated to the necessary temperature.

Use of finely dispersed systems (hundreds of Å) and highly homogeneous precursors prepared by cryochemical techniques allowed HTSC phases which are not easily prepared by other techniques to be obtained. Thus the Bi-2223 phase was synthesized from a 'cryochemical' precursor after 12 h of annealing⁵¹ (cf. 200–300 h annealing using traditional technologies), and the Y-124 phase was prepared without the use of a high pressure (up to 100 atm) of oxygen,^{49,52} which is normally necessary.

A comparison of the kinetics of phase formation of the Bi-2223 phase from different precursors allowed the following series of precursor activity to be established:⁵³ cryochemical technique (nitrates) > thermolysis of solutions (nitrates) — > citrate technique > ceramic technique. As expected, precursors without carbonates have an advantage, and for salts having the same chemical nature the advantage lies with the technique that allows a greater degree of homogeneous mixing of components (Fig. 9).⁵⁴

Conclusions

In this article we have tried to discuss the advantages (and disadvantages) of an array of chemical routes for HTSC powder preparation. Summarizing, one can conclude that the advantages of chemical routes, compared with the conventional ceramic route, are most often exhibited by: (a) lower temperatures and times of heat treatment for preparation of single-phase samples; (b) the possibility of synthesis of phases which cannot be prepared directly by the ceramic route; (c) more chemical and granulometric homogeneity of the samples; and (d) better physical (electric and magnetic) properties of HTSC ceramics.

Of the chemical routes one can also list preferences. In particular, the comparison of kinetics of phase formation of the Bi-2223 phase from different precursors allowed a series of precursor activity to be established.

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