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Influence of the Powder Characteristics on the Properties of the Bi-based Superconductors

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Abstract

Bi-based ceramic materials with superconducting properties were prepared using the solid state reaction technique, starting with reactive powders obtained via oxalate coprecipitation, as well as by the traditional powders route. The powder characteristics were evaluated using BET method and transmission electron microscopy (TEM). The stages of the high T_c supeconducting phases formation process were investigated by TG, DTA, XRD and IR methods. The dependence of the electric resistance versus temperature was recorded. The densities of the obtained samples have been also determined. The results emphasised high reactivity and shorter reaction times of the ceramic bodies obtained by the coprecipitation method. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Oxide superconductors require many problems to be solved before their application as polycrystalline bulk materials. Fine homogeneous powders are required to obtain densely, uniformly sintered bodies, as the densely sintered body probably has good superconducting properties.

The control of the particle size in high-T_c superconductors is of great importance, since for non-porous materials the particle size determines the surface free energy. All particle size translates into high surface free energy, which is the driving force for sintering into solid bodies. In addition, the use of small superconductor particles greatly facilitates processing method as screen printing, photolithography, etc. Particle size reduction may be achieved by grinding or milling, but this approach has several inconvenient. Most milling techniques involve solid media, which themselves are subject to attrition, leading to contamination of the superconducting powder. Secondly, it is difficult to active submicron particle size by mechanical milling processes. Thirdly, mechanical milling can lead to a degradation of the superconducting properties of the powder.

Many researchers into HTSC technologies have been connected with the development and application of chemical techniques for the preparation of precursors powders. Wet chemical methods have been extensively used in the preparation of high temperature Bi ceramic superconductors, to increase the reactivity of precursors powders. The main chemical methods include coprecipitation (oxalates, carbonates, citrates, etc.), complex formation (i.e. with EDTA) and sol–gel techniques. The oxalate route is one of the most promising chemical methods for the synthesis of high T_c superconducting materials.[1–4]

The solution chemistry of oxalate coprecipitation of Bi, Sr, Ca, Cu has frequently been used in the synthesis of this system. The main factors are the reagent for the pH adjustment, the obtaining of the quantitative coprecipitation and the elimination of the undesirable cations in the final oxalate coprecipitate.

The aim of the present work is to explain the potential of the oxalate coprecipitation route and to highlight the specific features of this method used in the preparation of HTSC powders. For comparison it was used the classical way of the ceramic method.

2 Experimental Procedures

2.1 Oxalates preparation
The coprecipitation method has been realised according to the procedure described in a previous paper.[5]

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Individual and four components Bi, Sr, Ca, Cu oxalate precipitates were carried out. The precipitation was realised by pouring the solution containing the metal ions in another containing 1M oxalic acid, used as a precipitant. Solution of 1M sodium hydroxide was used as a neutraliser to adjust the pH value of the obtained suspension to an optimal value ($pH = 3.5$), required by quantitative coprecipitation of all metals. The obtained precipitate was filtered out from the solution and carefully washed, to eliminate residual sodium from coprecipitate. The quantitative coprecipitation was checked by spectral analysis of the solution resulted after coprecipitate filtration.

2.2 Classic preparation

Oxides (Bi_2O_3, CuO) and carbonates ($SrCO_3$, $CaCO_3$) of high purity were used as raw materials. The mixtures were homogenized in an agate mortar for a period of 6 h. The material as obtained has been pressed and precalcined at 700, 750 and 800°C for 20 h. Prolonged annealing treatments (860°C/24 h) were used to obtain ceramic bodies with superconductive properties.

3 Results and Discussions

In the experimental conditions presented before, the quantitative precipitation of the Bi, Sr, Ca, Cu mixture was achieved. The concentration of the cations Bi, Sr, Ca, Cu in the residual solutions (after the precipitates filtration) was checked by spectral analysis. One may notice that Cu and Bi-oxalates are practically insoluble in the experimental conditions, Sr-oxalate being the most soluble

in good agreement with Zhang *et al.*'s[1] previous observation. The surface area of the powders was determined by BET measurements. The initial powders obtained by coprecipitation presented the surface area in the range of 30–32 $m^2 g^{-1}$. After 1 h annealing at 600°C, as the results of the reaction processes, the surface area of the powders decreased in the range of 5–7 $m^2 g^{-1}$. In any case of the classic ceramic processing steps, the surface areas of the powders were greater than 1 $m^2 g^{-1}$.

The average particle size and distribution, presence of the different phases and the shapes of the particles were evaluated by transmission electron microscopy, (TEM). TEM micrographs of the powders obtained as a result of the mentioned routes, before and after thermal treatments are presented in Fig. 1. One may notice the homogeneous granulometric distribution of the oxalate coprecipitate. The majority of the crystals, stick-like shape, were included in the range of $(0.02 \times 0.2)(\mu) < (1 \times L) < (0.15 \times 0.6)(\mu)$. Classic mixed powders presented an evident agglomeration tendency of the small particles around the large ones. A large dimensional dispersion, $(0.5 \times 1.2)(\mu) < (1 \times L) < (3 \times 8)(\mu)$ underlines this feature of the powder in the last case. As the temperatures increased in the annealing schedule, mica-like crystals appeared and growth from $0.3\mu g < \Phi < 1.5\mu$ to $2.0\mu < \Phi < 4.5\mu$. The thickness was around tens of Å very small crystals, needles like ($\approx 0.05 \times 0.5\mu$), were observed at the edges of the plat crystals. Trace of unreacted materials was also present up to 600°C [Fig. 1(c)].

These observations are in good agreement with the X-ray diffraction data presented in Table 1. The identified phases were approximately the same
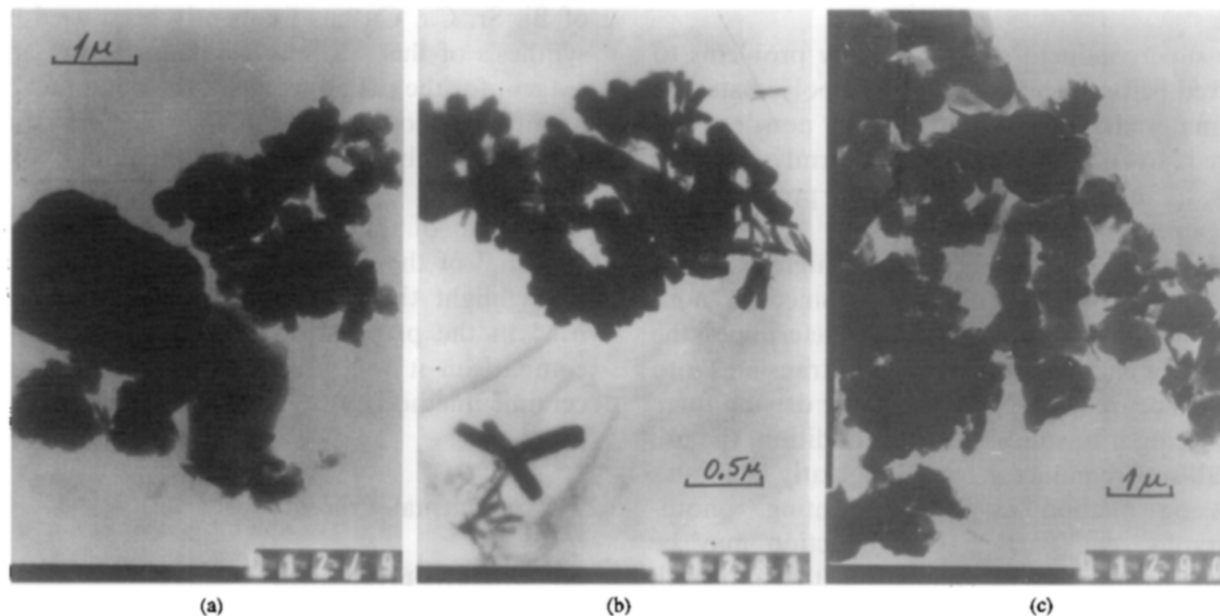

(a)   (b)   (c)

Fig. 1. TEM micrographs of (a) the classic and (b) coprecipitate routes obtained samples and (c) thermally treated coprecipitate at 600°C/1 h.

Table 1. The phases identified after the thermal treated samples

Samples			Phases		
	600°C/1 h	750°C/4 h: 750°C/20 h[a]	800°C/4 h: 800°C/20 h	850°C/4 h: 860°C/24 h
Oxalates	CuBi$_2$O$_4$, CUO α-Bi$_2$O$_3$, Sr$_{1x}$Ca$_x$CO$_3$	2201, CuO, SrCO$_3$	2212, CuO	2212, 2223, CuO(trace)
Classic	—	2201, CuO, SrCO$_3$	2212, CuO(trace), UL[b]	2212, 2223, UL

[a]Annealing for classic samples.
[b]UL, unidentified line(s).

in both cases at temperatures above 750°C. On emphasised that this was a result of some different reactions that took place at temperatures up to 600°C. Thermal analysis, presented in Fig. 2 underlined this observation.

The DTA/TG analyses were carried out in nonisothermal conditions. The XRD analyses have been used to identify the formed phases and to associate them with the effects on the DTA curves.

The DTA curves (Fig. 2) have generally different shape. The differences appear in the temperature range of 20–500°C. The thermal decomposition of the oxalates is accompanied by an exothermic effect [curve (a)] due to the overlapping of the endothermic effect of the decomposition with the exothermic effect of the CO oxidation to CO$_2$.
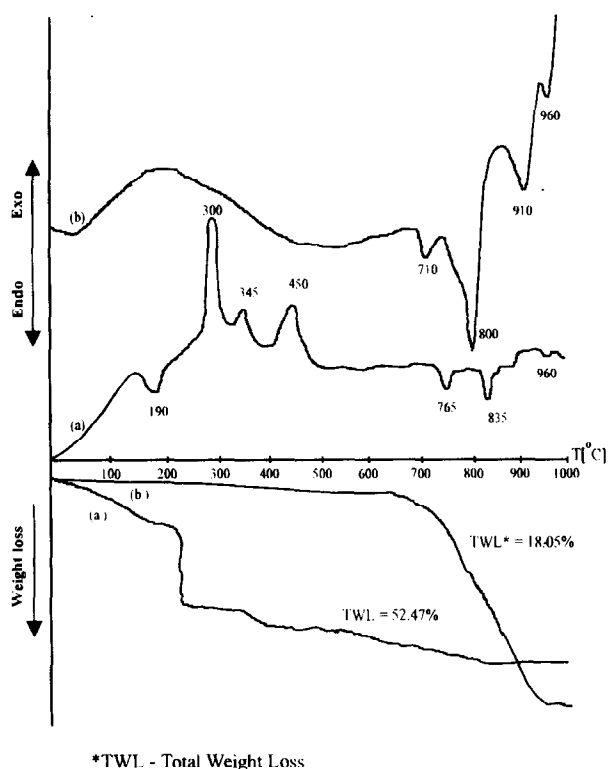

*TWL - Total Weight Loss

Fig. 2. DTA/TGA curves of (a) oxalate coprecipitates and (b) classic mixed powders of nominal composition Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_x$.

Bi and Cu oxalates decompose at about 300°C and Ca, Sr oxalates decompose at about 400°C. The thermal effects noticed in the case of the individual oxalates can be observed in the case of the four components coprecipitate too. The thermal decomposition of the oxalates is finished below 600°C.

The first effect at 710°C on curve (b) is attributable to the reaction between Bi$_2$O$_3$ and Ca and Sr oxides resulted as a consequence of decarbonation process. For curve (a) these effects were not observed.

At temperatures above 750°C the positions of the endothermic effects were systematically shifted to lower values for oxalates precursors. The main endothermic effect up to 800°C appears as a result of the complex process taking place: the 2201 phase formation, the continuation of the decarbonation process, the eutectic melt in the system Bi$_2$O$_3$–CuO, etc. The last area, delimited within the range 800–960°C, encloses endothermic effects that differ by the intensity and can be attributable to the melting process of the 2201 phase, polymorphic transformation and continuation of the decarbonation of SrCO$_3$ and to the reaction between resulted SrO and CuO. The last endothermic effect at 960°C for both cases is correlated with the melting of the system. The effect of the atomic level mixing, however, has a dramatic outcome on the reactivity of the powders as shown in the (Fig. 2), which is a comparison of the thermogravimetric profiles of the precursor–oxalate powders (a) and a physical mixture of carbonates and oxides (b).

The continuous and complex process of decarbonation was also inferred by the IR spectroscopy. Figure 3 presents a comparison between the materials prepared as previously described, after 600°C 1 h treatment [curve (a)] and an isothermal annealing up to 750°C [curve (b)]. The broad band observed for both samples was associated with the asymmetric vibration of the CO$_3^{2-}$ that belongs to CaCO$_3$ and SrCO$_3$. The peaks observed also at around 870 cm^{-1} (out of plain vibration) and 710 cm^{-1} (bending vibration) are assigned to
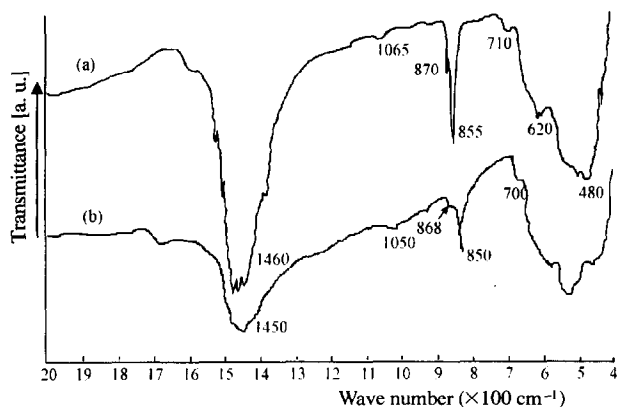
Fig. 3. IR spectra of Bi–Sr–Ca–Cu oxalate after 600°C/1 h (curve a) and mixed powders thermally treated 20 h at 750°C (curve b).

Fig. 5. Resistivity versus temperature dependance for (a) oxalate and (b) classic routes prepared samples.

CO_3^{2-} of $CaCO_3$, while those at 850 and 700 cm^{-1} are characteristic to $SrCO_3$. The weak peak at around 1050 cm^{-1} is specific to the last carbonate. It can be noticed that a similarity of the curves for both materials was observed in spite of the difference of the applied thermal treatment. The profile of the curves infers that the decarbonation process is more advanced for curves (b), but is a normal consequence of the higher temperature reaction. Meanwhile, the position of the vibration bands on curve (a) confirmed the existence of the carbonates solid solutions. In the range of 400–650 cm^{-1} the profile of the curves is a result of the overlapping of the vibrations characteristics of metal–oxide bond presented in the samples.

The samples mentioned above were also characterized from the point of view of density (Fig. 4). As a result of the different kinetic and mechanism of reactions, the maximum values for the density, in the case of oxalates precursors, were obtained at 800°C. Above this temperature the densities are very similar. The main observation we can mention is that this behavior is obtained for annealing treatments five times shorter than the classic route. The tendency of decreasing of the densities can be explained by the 2212 and 2223 phases formation. The bidimensional development and random orien-
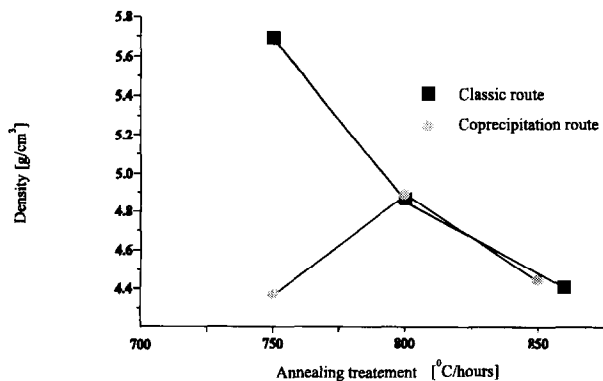
tation of these crystals confirm this phenomenon. This observation is in good agreement with the XRD analysis.

The resistivity variation vs. temperature was recorded, using the four-points measurement technique. The results were shown in Fig. 5. One can notice an alteration of the curve profile at around 110 K—due to the high-Tc phase transition. An other changing in the $R(T)$ curves profile was observed around 85 K due to the beginning of the second superconductive transition ($T_c^{ons}2212$). The transition temperature $T_c(R=0)$ was not reached for any samples. These results were in good agreement with the XRD analysis. Prolonged annealing treatments are required in both cases.

4 Conclusions

The oxalate coprecipitation method represents a sure and easy way to prepare superconducting phases in the Bi–Sr–Ca–Cu–O system. In order to obtain pure high-T_c superconductive phase optimal and prolonged thermal treatments are required.

The formation of a solid solution of Sr–Ca–carbonate and the facile formation of Cu–Bi–oxide indicate the high level of mixing at the 'atomic level' attributable by the coprecipitate oxalate method. The kinetic of the reactions was also enhanced.

The results emphasised high reactivity and shorter reaction times of the ceramic body obtained by the coprecipitation method.

Fig. 4. Density versus annealing treatment dependence.

References

1. Zhang, Y., Fang, Z., Muhammed, M., Rao, K. V., Skurnryev, V., Medelius, H. and Costa, J. L., The synthesis of superconducting Bi compounds via oxalate coprecipitation. *Phys. C*, 1989, **157**, 108–114.
2. Zhang, Y., Muhammed, M., Wang, L., Nogues, J. and Rao, K. V., Synthesis of superconducting Pb/Sb doped

BiSrCaCuO compounds via oxalate coprecipitation. *Mat. Chem and Phys.*, 1992, **30**, 153–159.

3. Wang, L., Zhang, Y. and Muhammed, M., Synthesis of nanophase oxalate precursors of YBaCuO superconductor by coprecipitation in microemulsions. *J. Mater. Chem.*, 1995, **5**(2), 309–314.

4. Medellus, H. and Rowcliffe, D. J., Solution routes to synthesize superconducting oxides. *Mat. Sci. and Eng*, 1989, **A109**, 289–292.

5. Marta, L., Zaharescu, M., Clontea, L. and Petrisor, T., Chemical route to the synthesis of superconducting bismuth oxide system. *Appl. Superconducylvity*, 1993, **1**, 677–691.