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TEM and SEM studies on the formation of superconducting phases in the Bi-based system

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Abstract

We present the formation mechanism and structure of the superconducting phases in the Bi–Sr–Ca–Cu–O system by TEM and SEM observations. Oxalate coprecipitation was used as preparation method. The average particle size, distribution and the presence of different phases and shapes of the particles were evaluated. All samples were well crystallized, showing grains in submicronic range. After thermal treatments, the complex samples showed mica-like crystals uniform dispersed and also an orientation tendency. The superlattice was composed of building blocks and successive planes. The TEM observations were in agreement with the diffraction patterns that revealed a mixture of 2212 and 2223 superconducting phases. With the building blocks in the system, it is possible to form many incommensurate phases that destroy the symmetry. Careful control of the preparation conditions is essential to produce a well-ordered commensurate phase, suitable for the precise determination of the complete superstructure by X-ray diffraction. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Bi–Sr–Ca–Cu–O system; Oxalates; Structure of superconducting phases; TEM and SEM observations

1. Introduction

The desire to achieve uniform, fine ceramic powders has generated a wide variety of methods for the preparation of powders, among them wet chemical methods being the mostly used, as they increase the homogeneity of the product during the synthesis stages.[1] The coprecipitation method is one of the known wet chemical routes most commonly used in the synthesis of high temperature superconducting oxides,[2] leading to an intimate mixing of the components that cannot be obtained by grinding. Coprecipitation is easy to perform, but requires a careful approach in order to produce a chemically homogeneous precipitate with the desired composition.[3] The success of the synthesis strongly depends on the control of the solution chemistry at every stage of the process. Based on literature data there are two ways of approaching the oxalate coprecipitation for the Bi-based superconducting materials synthesis: coprecipitation in a basic range of pH [4–8] and in an acid range of pH.[9–13] The coprecipitation in acid range leads to a precipitation of all metal ion species as oxalates, but reaching an optimum value of pH in order to achieve a quantitative precipitation still is a controversial problem of the method. The coprecipitation in basic range is less sensitive to the pH value, but leads to a mixture of coprecipitates that behave differently in the subsequent thermal decomposition processes. Also, the possibility of the absorption of a quantity of alkali ions in the final precipitate exists, or even of forming some insoluble double salts.

A lot of interest was focused on elucidating the origin of the superconductivity at high temperature. Most advanced ceramics can be obtained starting from raw materials which quality is of major importance in order to obtain the desired materials. There have been many attempts to study the microstructure of the initial powders, as well as the thermally treated materials in order to obtain a Bi-based superconductor by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements. The Bi-based system microstructure was characterized by TEM by Carim et al.[14] SEM studies were realized by Zhang et al.[9] for the oxalates coprecipitates, by Spencer[6] for a $pH = 8$ precipitated material using a synthetic route via coprecipitation of oxides and precursors such as hydroxides and carbonates and by Ruiz et al.[15] for a Bi-based system obtained by sol–gel method and polymer reaction. Constantinescu et al.[16] studied by SEM the same

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system doped with Sb and Pb, for samples obtained via oxalate, citrate, acetate and nitrate. TEM and SEM micrographs for a Pb doped Bi-based system prepared at pH of 6.7 starting from nitrates coprecipitated with oxalic acid were made by Chiang et al.[10]

In previous works a systematic study of the high-T_c Bi-based superconductors preparation was performed, using the oxalate route as a coprecipitation method.[13] In the present paper we focused our studies on TEM and SEM determinations in order to establish the influence of the preparation method on the initial powders size and reactivity. A systematic TEM study of the evolution of the starting oxalates coprecipitates microstructure in order to obtain a 2212 and 2223 containing material was realized. The powders morphology and homogeneity have been examined by SEM, which revealed the shape, size distribution of crystals and the compositional consistency among various particles of the precipitates. However, the chemical homogeneity of the particles agglomeration determination is limited by the SEM resolution limit.

2. Experimental

2.1. Powder preparation

Individual Bi, Sr, Ca, Cu oxalates as well as four components mixture were prepared using stoichiometric amounts of starting materials corresponding to the formula $Bi_2Sr_2Ca_2Cu_3O_y$. The way of approaching the coprecipitation method in order to synthesize the superconducting material and the applied thermal treatments were discussed in previous papers.[13,17,18] Precise control of the phase content of the samples is required for the initial nominal composition.

2.2. The characterization of the oxalates and the thermally treated samples

Both starting and thermally treated samples were characterized by X-ray diffraction (XRD), TEM/ED (electron diffraction) and SEM observations, BET and density measurements. The coprecipitated powders as well as the thermally treated samples were investigated by transmission electron microscopy using a JEOL transmission electron microscope operating at 200 kV. Particles from powder material or crushed pellets were dispersed in a solution of formvar in alcohol on a glass plate. Particle morphology was monitored with a Carl Zeiss Digital Scanning microscope 942. The structure of the obtained materials was determined by XRD and ED. The X-ray diffraction patterns were recorded with a TUR-M62 equipment with a HZ 63 θ-2θ diffractometer using CuK_α radiation. For the determination of the specific surface area, the BET method was used with a volumetric apparatus by absorption of nitrogen at liquid nitrogen temperature. The skeletal density of the raw powders was measured by He pycnometry.

3. Results and discussion

Based on literature data, a full, stoichiometric quantitative coprecipitation of individual oxalates and BiSrCaCuO mixture was studied in acid range of pH, at the value of 3.5. To obtain a good stoichiometry of the material, in our case, the pH value determined the complete and quantitative coprecipitation of all components and was established by previous experimental and theoretical works.[13,17,18] The concentration of the cations Bi, Sr, Ca, Cu in the solution remaining after precipitate filtration was checked by spectral analysis and presented in a previous paper.[14] Cu and Bi oxalates are practically insoluble in the experimental conditions used; Sr oxalate is the most soluble, observation in agreement with Zhang et al.[9] previous observations, who considered that an excess of $Sr(NO_3)_2$ could be necessary in order to achieve a quantitative coprecipitation of Sr as oxalate. We avoided in our synthesis an excess of Sr nitrate, working with more concentrated solutions (1 M) and less dilution of the final coprecipitate. The full quantitative coprecipitation of all individual oxalates at the same value of pH was confirmed once more by the much lower ionic content in the residual solution remaining after the filtration of the four components coprecipitate, as previously demonstrated.[13]

3.1. TEM investigations

A systematic TEM study was realized on the starting individual oxalates of Bi, Sr, Ca Cu, and the raw oxalate mixture and also on the thermally treated material up to 850°C.

3.1.1. TEM results for the individual oxalates and the four component coprecipitate

TEM studies of the individual oxalates of Bi, Sr, Ca, Cu were made and a full detailed discussion of the results were presented[19]; all particles in the samples exhibited sizes in the micron range and nevertheless, the platelet size and shape were observed to be homogeneous throughout the bulk of the material.

The Bi oxalate consists of well-defined platelets with polygonal shape, well crystallized, uniform, with an average size of 1.02 μm and a high porosity. The Sr oxalate presents a porous platelet-like shaped phase with average diameter of the particles of about 1.35 μm. Porous platelets (~80%) with an average diameter of 1.4 μm, uniform and with rounded off margins were obtained for the Ca oxalate. The Cu oxalate, extremely unstable in the electron beam, has a special behaviour: it rapidly changes into a mixture of Cu and CuO as it could be noticed during the TEM measurements and in good agreement with the results of ED that certifies two types of structures: the presence of 95% of reacted material from which 75% is CuO with particle size from 0.08 to 0.2 μm and 25% metallic Cu with particles size from 0.015 to 0.08 μm. The results are in good concordance with the DTA/TG and XRD results of Cu oxalate that evidenced decomposition to metallic Cu and re-oxidation to CuO.[13] The TEM and ED results evidence the different degree of crystallization for the individual oxalates.

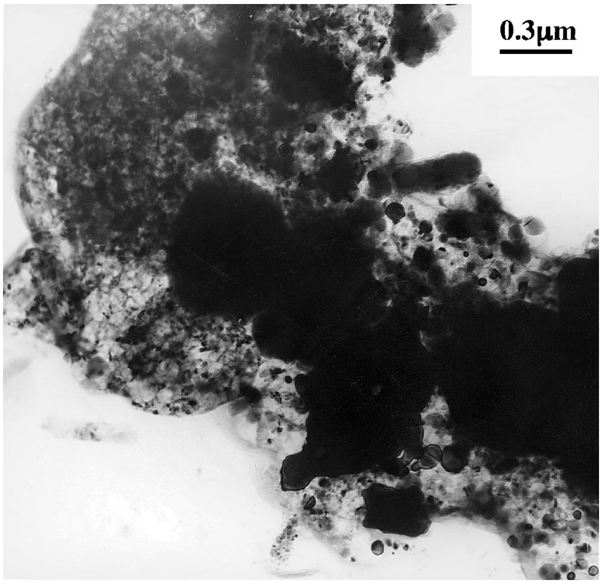


Fig. 1. TEM micrograph of the four-component coprecipitate.

In the case of the four-component coprecipitate, light-blue, well dispersed powders have been synthesized, with a specific surface area in the range of 30–32 m^2/g and a density of 2.2–2.4 g/cm^3. The powders appeared to be crystalline by XRD.[17] As TEM micrograph shows (Fig. 1), the four-component coprecipitate is crystallized, with well dispersed crystallites and regular shapes. All particles noticed for the individual oxalates are present in the four-component coprecipitate. Traces of amorphous phase are also present, which explains the agglomeration tendency of the material. A mixture of porous platelet shaped, big particles with diameters from 0.1 to 0.3 μm and small particles with dimensions from 0.001 to 0.6 μm are present. Around 8 out of 10 of the crystals can be included in the range of $(0.001\times0.2)<(l\times L)<(0.15\times0.6)$ μm. Some agglomerates with spherical shape and diameters between 0.05 and 0.5 μm are identified as traces of metallic Cu. TEM microanalyses carried out on particles of the powders of individual and four component oxalates revealed that all starting oxalates have a similar behaviour. A high porosity of the particles could be noticed. A higher instability in the electron beam during the TEM measurements was registered for the individual oxalates that decomposed to the respective oxides when the beam was condensed onto the sample; when the four components

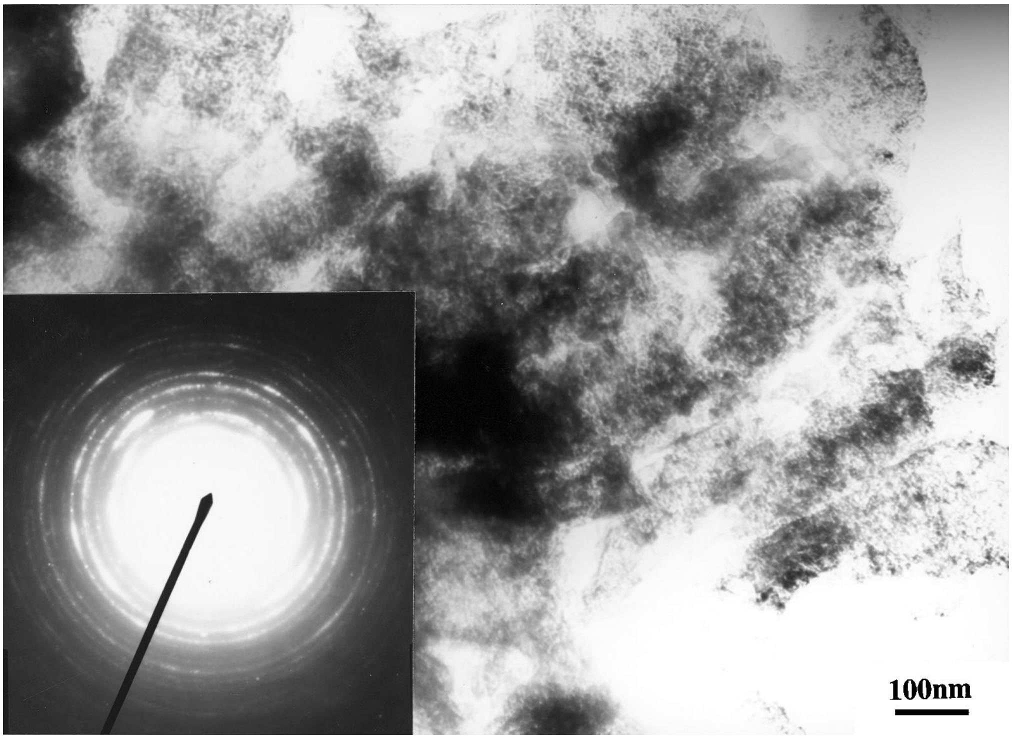


Fig. 2. TEM micrograph and ED pattern of the coprecipitate thermally treated at 600°C/1 h.

are coprecipitated together a higher stability of the material in the electron beam was noticed.

3.1.2. TEM investigations for the thermally treated coprecipitate

Fig. 2 displays a TEM micrograph of the coprecipitate decomposed at 600°C. The material is well crystallized, with individual grains in the submicron region. The crystallites are well dispersed, with a homogeneous granulometric distribution, stick-like and plate-like shaped and main dimension $l \times L = 0.1 \times 0.3$ μm. The presence as major phase (∼70–75%) of the crystallites with average dimension proves the homogeneity of the materials. The TEM microanalysis of the four-component coprecipitate supports the idea of the presence of all types of crystals noticed for the individual components and a lower dimension of the crystals compared to the individual ones. The plate-like crystallites tend to agglomerate and possess an irregular polygonal geometry. The polygonal units that are not completely opaque into the electron beam show a thickness of tens of Å, with 0.3∼1.5 μm diameters for stick-like shaped crystals. Very small needles-like crystals, ($\sim 0.05 \times 0.5$μ), were also observed at the edges of the platelet-shaped crystals. Traces of unreacted material were present up to 600°C. The ED indicates the presence of the multiphase microcrystalline material and of the amorphous phase still present at this temperature. After the annealing treatment at 600°C, as a result of the reaction processes, the surface area of the powders decreased to the range of 5–7 m^2/g and the density measured was 2.5–2.7 g/cm^3, in good agreement with the TEM studies, which also revealed a high porosity of the material.

3.1.3. SEM results for the initial coprecipitate and the thermally treated coprecipitate

The morphology and homogeneity of the oxalate coprecipitate has been examined in SEM as shown in Fig. 3. The results revealed the individual particles size of the powders to be 0.1–0.4 μm and a certain extent of agglomeration. This is in good agreement with the values from the specific surface area and the skeleton density. SEM micrograph of the four components mixture material treated at 600°C is shown in Fig. 4. A strong tendency towards agglomeration is observed, with particles agglomerated to a mean size of 0.2 μm. The SEM of the coprecipitate reveals needle-like crystals with small particle size and a compositional consistency among various particles of the oxalate coprecipitate, indicating chemical homogeneity at least within the SEM resolution limit. We can conclude that SEM images helped to clarify some morphological aspects as the orientation of the grains. The changes in the morphology aspect of the particles for the thermally treated materials indicate the beginning of the reaction processes, as confirmed by XRD results.

3.1.4. TEM results of the 850°C thermal treatment

The TEM results of the 850°C thermally treated coprecipitate are shown in Fig. 5. The material is well crystallized with grains of tens of micrometers. A good and uniform dispersion of the particles as mica-like crystals and an orientation tendency could be noticed. The superlattice is composed of building blocks and successive planes, results in good agreement with XRD patterns that revealed the presence of 2212 and 2223 superconducting phases.[13] The blocks presence in the system could form incommensurate structures, which destroy the symmetry, so, a good control of the preparation method is essential in order to produce a commensurate and well-ordered phase procedure in the system, suitable for complete superstructure determination by XRD.

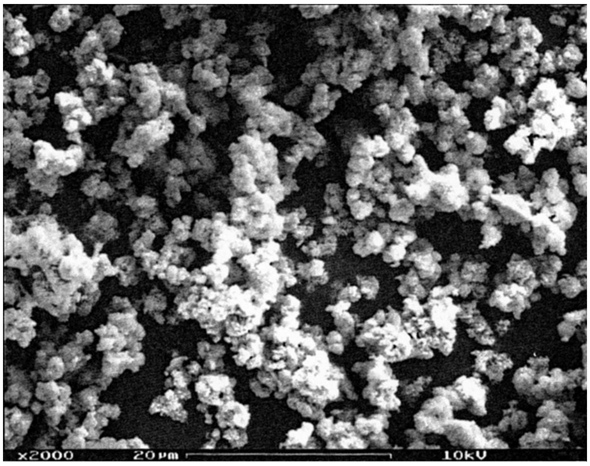


Fig. 3. SEM micrograph of the initial four-component coprecipitate.

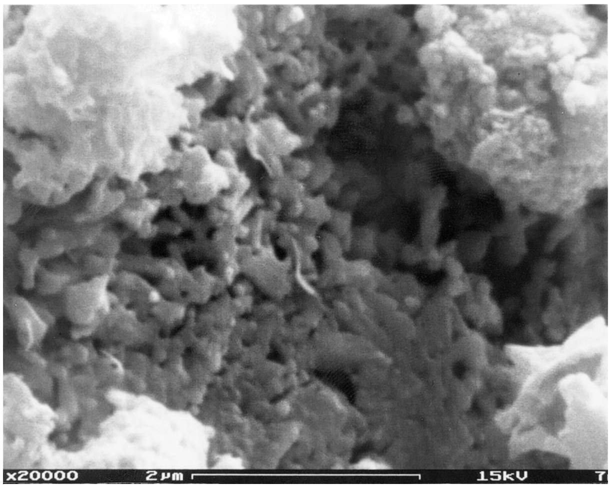
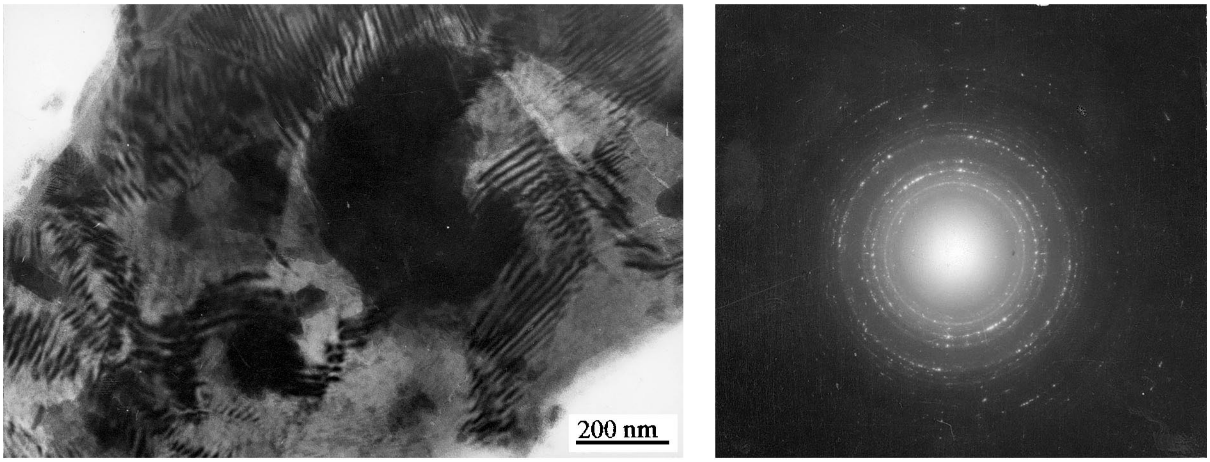


Fig. 4. SEM micrograph of the thermally treated coprecipitate at 600°C/1 h.



(a) (b)

Fig. 5. TEM micrograph and ED pattern for the coprecipitate thermally treated at 850°C/4 h.

4. Discussion and conclusions

Individual oxalates of Bi, Sr, Ca, Cu were obtained with particles size ranging between 1.02 μm for Bi oxalate, 1.35 μm for Sr oxalate, 0.2–1.4 μm for Ca oxalate and 0.015–0.2 μm for Cu oxalate. All samples were crystallized, with porous crystallites, also containing a significant amorphous phase according to the ED data, which confirm the previous XRD results.[13,17] Cu oxalate is the most unstable; it decomposes in the electron beam leading to the formation of a Cu and CuO mixture, behaviour evidenced also in DTA measurements. Working in an acid range of pH, using 1 M concentration and low dilution of the starting solutions, microcrystalline coprecipitates have been obtained with a tendency towards agglomeration very similar to those mentioned by Zhang et al.[10] The TEM microanalysis of the four-component coprecipitate supports the idea of the presence of all types of crystals noticed for the individual components and a lower dimension of the four-component mixture crystals as compared to the individual ones. A higher stability in the electron beam during TEM and SEM determinations was registered in the case of the four-component coprecipitate. By coprecipitation, a material with a higher crystallinity was obtained compared to other results from the literature,[8,9] but also with higher reactivity; the thermal treatment at 600°C, applied to decompose the initial oxalate, generated very reactive powders, with high porosity and small particles as well, observations highlighted by the TEM and SEM results. We can assume that the high reactivity of the obtained powders can be related to the high porosity of the crystals. Crystalline powders with small particles, in submicronic range, porous, but with a high reactivity were obtained by oxalate coprecipitation. Nevertheless, electron diffraction patterns show the presence of amorphous phase residues causing the characteristic halos till 600°C. The features of the final material obtained by the oxalate route presented good superconducting properties, similar to those obtained in the literature.[9] We produced homogeneous, submicronic particles of oxalate precursors generating powders containing 2212 and 2223 phases after short thermal treatments. Our material presented a 108 K phase and was obtained under much more amenable heat treatment conditions. In order to obtain single 2223 phase, prolonged thermal treatments are required, as between 24 and 80 h at 850 and 865°C, previously reported.[5,7,8,10,12] The TEM and SEM results highlight the effect of mixing at the atomic scale level and how chemical homogeneity can be attained on this level in a multicomponent system via the oxalate coprecipitation method.

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