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Reactivity of the Bi, Sr, Ca, Cu Oxalate Powders used in BSCCO Preparation

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Abstract

The solution chemistry of oxalate coprecipitation of Bi, Sr, Ca, Cu has frequently been used in the synthesis of Bi-based ceramic systems, although there are different opinions referring to some major aspects, such as coprecipitation pH and precipitating agent. In the present work we established the precipitation conditions of Bi, Sr, Ca, Cu individual oxalates and of the quaternary mixture. The initial and thermally treated oxalate powders were characterized by XRD, IR, BET methods and TEM observation. The decomposition conditions were established based on a DTA/TG study. The powders resulted from the decomposition of Bi and Cu oxalates contain the corresponding oxides and the Ca and Sr oxalates decomposition lead to the carbonates obtaining. In each case a high reactivity and a very small powder particle size were observed. A very good powder homogeneity has also been noticed in the final mixture of oxalates. Compared to superconducting ceramic materials realized by a classic route, the reactive oxalate powders allow the decrease of both thermal treatment periods and temperature, emphasizing a high microstructure homogeneity of the ceramic body. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Numerous studies are concerned with the improvement of the reaction kinetics and the preparation of the BSCCO high-T_c material. The BSCCO is a complex system that contains phases with complex structures. It is very well known that the superconducting phases 2212 ($T_c = 85$K) and 2223 ($T_c = 110$K) are obtained stepwise. Some strategies were employed to obtain the high-T_c phase, which is known to be very difficult to obtain.

Two major aspects are taken into account referring to the synthesis of a high-T_c superconducting material: the substitution and the preparation method of the precursors.

Substitution of various ions in cuprate oxide superconductors represents an important experimental technique in the obtaining of high T_c superconductivity. Special attention was paid to the dopants on the formation mechanism and structure of the superconducting phases in the BSCCO system.

At the same time, much research into HTSC technologies has been connected with the development and application of chemical techniques for the preparation of precursors powders.[1,2]

Wet chemical methods have been used extensively in the preparation of high temperature Bi ceramic superconductors, in order to increase the reactivity of precursors powders. The main chemical methods used, include coprecipitation (oxalates, carbonates, citrates, ...), complex formation (e.g. with EDTA), and sol–gel techniques. Among these, the oxalate coprecipitation is frequently used to obtain high quality precursor powders for Bi superconductors.

The oxalate route is probably one of the most promising chemical methods for the synthesis of high T_c superconducting materials.[1–4] It can produce highly homogeneous powders that consist of individual particles smaller than 100 nm[3].

To obtain well-dispersed powders, the control of the growth and aggregation of the primary particles during the coprecipitation process is of great and essential importance.

The solution chemistry of oxalate coprecipitation of Bi, Sr, Ca, Cu has been used frequently in the synthesis of Bi-based systems, although there are different opinions referring to some major aspects: the coprecipitation pH and also the precipitating agent.

An important contribution has been the reagent for the pH adjustment. It is very important that in the final oxalate coprecipitate undesirable cations

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are not found (which is strongly dependent on the reagent type used) and that the quantitative coprecipitation is realized.

Previous studies concerning the oxalate coprecipitation in the BSCCO system have been realized by Zhang *et al.*[1]

The precipitation was carried out at a pH value of around 5. They also specified that the composition of the formed oxalate precipitates is practically insensitive to pH value in a relatively wide range (pH = 3·5–6·5). They observed improvement in the superconducting properties as indicated by the resistivity data for the samples from oxalate precursors and that the homogeneous oxalate precursors show the feature of producing a superconductor with higher T_c as compared to those produced by dry methods.

Medelius *et al.*[4] report that the solution routes offer the high degree of control of particle size, shape and distribution, but the control of solution chemistry is essential at every stage of the process.

Marbach *et al.*[5] also studied powders preparation along the wet chemical oxalate route. They noticed that the solubilities of Ca-, Sr-, Cu-, Bi-oxalates depend on the pH value and realized the precipitation with $[N(CH_3)_4]_2\ (C_2O_4)/N(CH_3)_4OH$ and kept the pH value at 12 by adding $N[(CH)_3]_4OH$.

In the work of Constantinescu *et al.*,[6] high-T_c superconductor is synthesized using oxalates, citrates acetates and nitrates as starting materials. The best samples containing the highest portion of the 2223 phase have been obtained by the nitrate decomposition route. It has been proved that oxalates, citrates and acetates lead to very sinterable powders.

The importance of chemical routes for the preparation of high temperature superconducting powders is discussed by Metlin *et al.*[7] As expected, the process of coprecipitation has a few advantages: high homogeneity achieved by coprecipitation and the absence of melting by thermal treatment, which allows the formation of a single-phase product to be obtained more rapidly.

Three alternative routes of the oxalate method for synthesis of the high-T_c superconducting BSCCO have been studied by Aldica *et al.*:[8]

- a simultaneous precipitation of all metallic components with oxalic acid was realized and the pH value was adjusted with NH_4OH to pH = 5·5–6;
- another way was to obtain each component by a complete and individual precipitation; the oxalates were mixed at a pH of about 2–3 and then the pH was adjusted to 5·5–6 using NH_4OH;
- the third case consisted of the precipitation of the oxalates as groups of metals Ca and Sr at pH = 7, Cu, Bi, Pb at pH = 3·5–4, and than the pH of final mixture was adjusted to 5·5–6. The best results were obtained in this way.

Zaharescu *et al.*[9–12] used oxalate coprecipitates in order to obtain high quality precursors powders for Bi-based superconductors. The quantitative coprecipitation was realized at a pH value of 3·5.

Based on the results obtained by Marta *et al.*,[13] the conditions of quantitative precipitation in order to obtain precursors for superconducting powders were studied.

The experimental studies confirmed by the theoretic results and based on the diagrams obtained by a computation program offered the possibility of optimal conditions of coprecipitation for chemical preparation of oxide superconductors from the BSCCO system.

In the present work, from the solubilities curves, the optimum value of coprecipitation pH of Bi, Sr, Ca and Cu cations is 3·5 for an oxalate 0·1 M excess.

The aim of the present examination is to clarify some of the items from the techniques used in the papers mentioned above, to explain the potential of the different ways of approaching the chemical method of oxalate coprecipitation and to highlight the specific features of their use in the preparation of HTSC powders.

2 Experimental

2.1 Oxalates preparation

Individual and four components Bi, Sr, Ca, Cu oxalate precipitates were prepared.

An aqueous 1 M nitrate stock solution was used as a starting precursor.

The precipitation was carried out by pouring the solution containing the metal ions in another containing 1 M oxalic acid, used as a precipitant. A solution of sodium hydroxide was used as a neutralizer to adjust the pH value of the obtained suspension to an optimal value (pH = 3·5), required by quantitative coprecipitation of all metals.

Special attention was paid to the Bi solution preparation. This solution can be prepared by dissolving $Bi(NO_3)_3$ in nitric acid instead of water, being careful to avoid the precipitation of basic Bi nitrate $Bi(OH)_2NO_3$ as a function of the solution dilution.

Adding an excess of Sr as $Sr(NO_3)_2$ is also required because of the relatively high solubility of Sr oxalate.

A combined glass electrode was used to measure the pH of the solution under stirring. The obtained precipitate was filtered out from the solution and carefully washed in order to eliminate residual sodium from the coprecipitate.

The quantitative coprecipitation was checked by spectral analysis of the resultant solution after coprecipitate filtration.

2.2 The characterization of the oxalates and the thermally treated samples

The starting oxalate powders, as well as thermally treated samples, were characterized by XRD, IR and BET methods, TEM observation and DTA/TGA.

The X-ray diffraction patterns were recorded with a θ-2θ diffractometer using CuKα radiation monochromatized by a flat graphite crystal placed before the scintillation detector. Flow chart records were used to determine the phase compositions of the samples.

IR spectra were recorded in the range 4000–400 cm^{-1} for the starting coprecipitates and in the range 2000–400 cm^{-1} for the thermally treated samples. A Carl Zeiss Jena-Specord 75 IR equipment was used.

The specific surface area of the powders was determined using a BET apparatus with nitrogen.

The coprecipitated powders were investigated by transmission electron microscopy using a TESLA BS-540 electronic microscope.

To establish the thermal events, DTA/TGA was performed up to 1000°C in air with Al_2O_3 as reference. A MOM OD-102 Derivatograph with a heating rate of 5°C/min was used.

According to the DTA/TG analysis results, the oxalate coprecipitate has been decomposed by thermal treatment at 600°C for 1 h in air. Disk-shaped samples ($\phi = 10$ mm and 1 mm thick) were obtained from the powders and subsequently treated for 4 h at the following temperatures: 750°C, 800°C, 850°C.

On the thermally treated samples, the ceramic properties were determined: porosity, linear shrinkage and density. The porosity was determined by weighing samples before and after 24 h immersion in toluene. The linear shrinkage was determined by measuring the diameter of samples before and after thermal treatment. The density was determined by hydrostatic method.

3 Results and Discussion

In the experimental conditions presented before the quantitative precipitation of individual oxalates and the coprecipitation of Bi, Sr, Ca, Cu mixture were achieved. The concentrations of the cations Bi, Sr, Ca, Cu in the residual solutions (after filtration of the precipitates) was checked by spectral analysis and are presented in Table 1.

One may notice that Cu- and Bi-oxalates are practically insoluble in the experimental conditions used, Sr oxalate being the most soluble according to the previous observation of Zhang *et al.*[1] In the case of the mixture of the four components, the final percentage of ion content is much lower.

By the oxalate coprecipitation, highly dispersed microcrystalline powders have been obtained. The XRD patterns of the individual and four components oxalate are presented in Fig. 1.

The XRD pattern of quaternary mixture shows a mixture of Bi-oxalate, Sr-oxalate, Cu-oxalate and (Ca, Sr) mixed oxalate as well as certain amounts of amorphous phase.

Table 1. Results of spectral analysis

Type of sample	*Ions (%)*	*Solution*	
		Initial solution	*After precipitation*
Bi-oxalate	Bi	20·9	0·0001
Sr-oxalate	Sr	8·8	0·60
Ca-oxalate	Ca	4·0	0·12
Cu-oxalate	Cu	6·4	0·051
BiSrCaCuO-oxalate	Bi	20·9	0·00055
	Sr	8·8	0·30
	Ca	4·0	0·022
	Cu	6·42	0·003

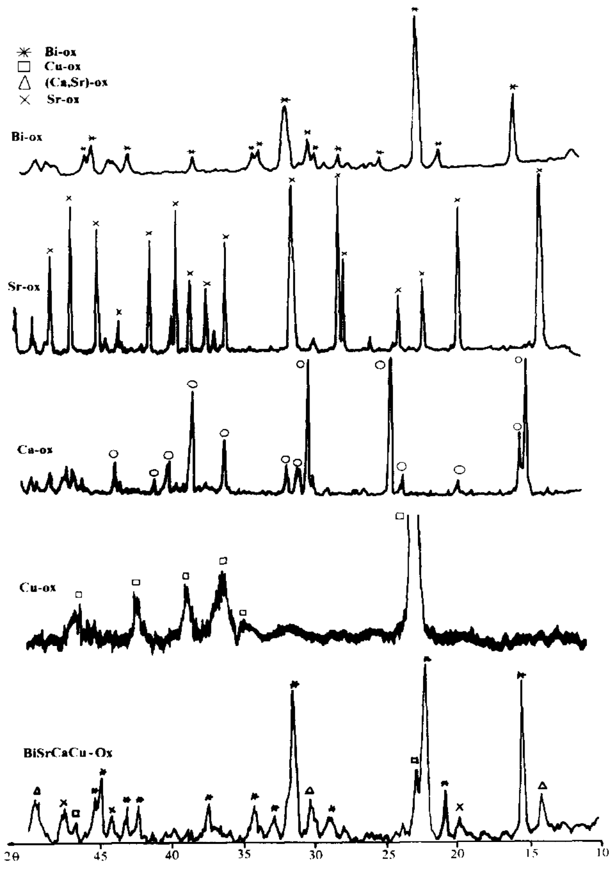


Fig. 1. XRD patterns of the individual oxalates and of four-components oxalates mixture.

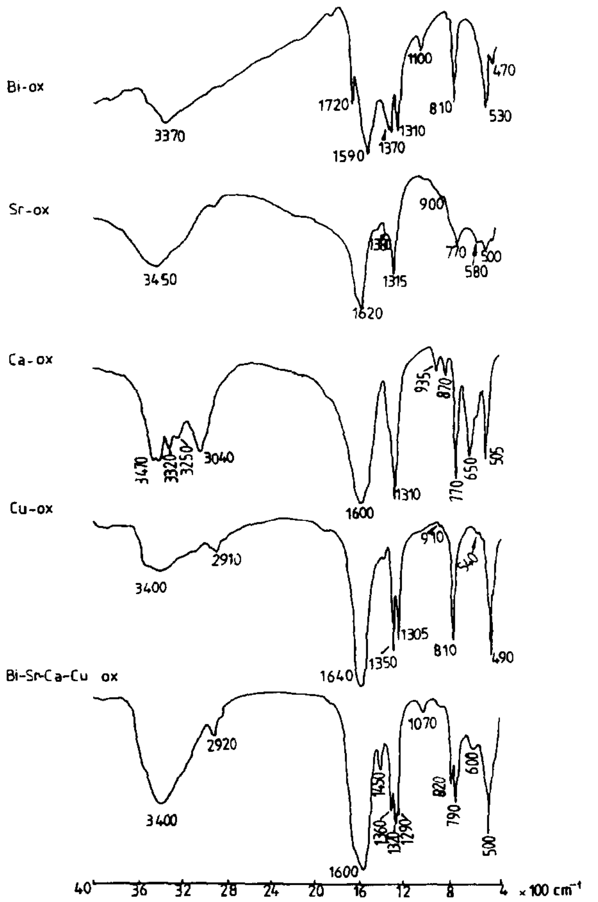


Fig. 2. The IR spectra of the individual oxalates and four-components oxalates mixture.

The assignment of the diffraction lines for the oxalates coprecipitates have been performed by comparison with ASTM files. The obtained XRD patterns for the individual oxalates are in good agreement with literature data.

The IR spectra of the individual oxalates and oxalates mixtures are presented in Fig. 2.

In the case of individual oxalates the characteristic bands of the oxalate group are evidenced: 1600 ($\nu_{s\ C=O}$), 1370–1290 ($\nu_{s\ C-O}$, $\nu_{s\ C-C}$), 900 ($\nu_{s\ C-O} + \delta_{O-C=C}$), 800 ($\delta_{O-C=C}$), 600 ($\nu_{s\ C-C}$) cm^{-1}.

The presence of the hydration water is noticed by the bands situated in the 3700–2900 cm^{-1} range. The M–O bond and the M–Oxalate bond are represented at: 800, 600 (ν_{M-O}) and 500 cm^{-1} (δ_{M-Ox}).

In the case of the oxalates mixture it was found tha the bands appear in the individual species spectra. An overlapping of the characteristic bands observed for the individual oxalates are noticed.

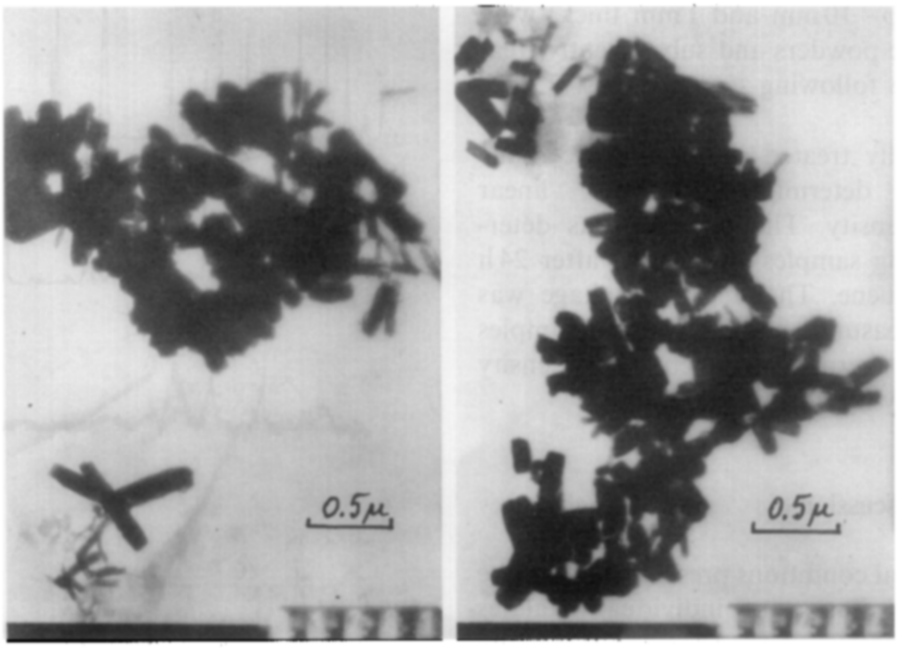
The powders obtained by coprecipitation presented the specific surface area in the range of 30–32 m^2/g.

In Fig. 3(a), (b) the TEM micrographs for the BSCCO starting sample are presented. It is observed that the sample is crystallized and that the crystallites and the individual grains are in the submicron range. The main dimension of the crystals are: $1 \times L = 0{\cdot}1 \times 0{\cdot}3\ \mu\mathrm{m}$.

Figure 4 shows the results of the thermogravimetric analysis TGA and differential thermal analysis DTA of the individual oxalates.

The major decomposition step is related to the loss of water, which is finished at 190–270°C, and the conversion of the precipitates into (Ca, Sr)CO_3, Bi_2O_3 and CuO between 320 and 490°C.

The thermal decomposition of the oxalates is accompanied by an exothermic effect due to the overlapping of the endothermic effect of the decomposition with the exothermic effect of the CO oxidation to CO_2.



(a) (b)

Fig. 3. TEM observation of the initial BSCCO sample.

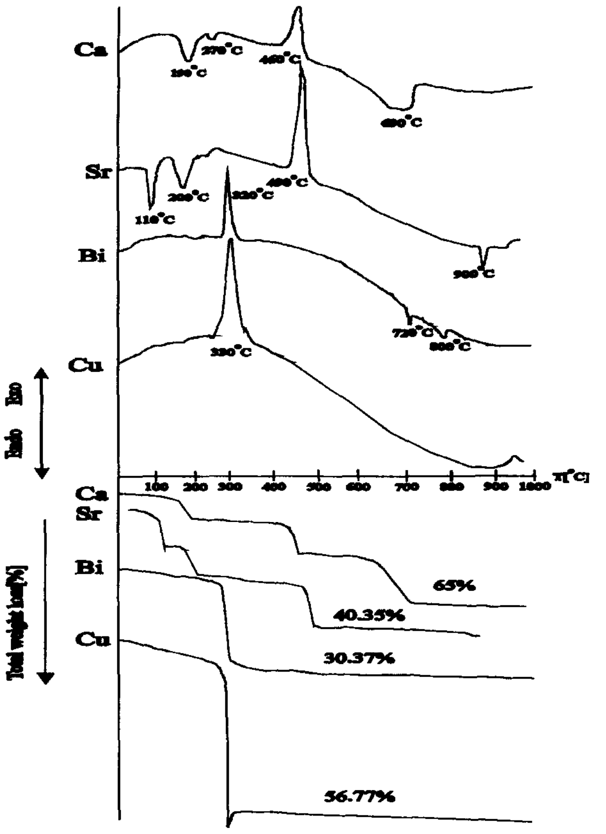


Fig. 4. DTA/TG curves for individual oxalates.

Bi- and Cu-oxalates decompose at about 300°C and Ca-, Sr-oxalates decompose at about 450°C.

Figure 5 shows the results of the thermogravimetric analysis TGA and differential thermal analysis DTA of the quaternary mixture of oxalates.

The thermal effects noticed in the case of the individual oxalates can also be observed in the case of the four-component coprecipitate. In all cases the thermal decomposition of the oxalates is finished below 600°C.

According to the DTA/TGA results of the starting materials, in order to realize the processing of high T_c ceramic material the initial oxalates were decomposed by thermal treatment at 600°C for 1 h.

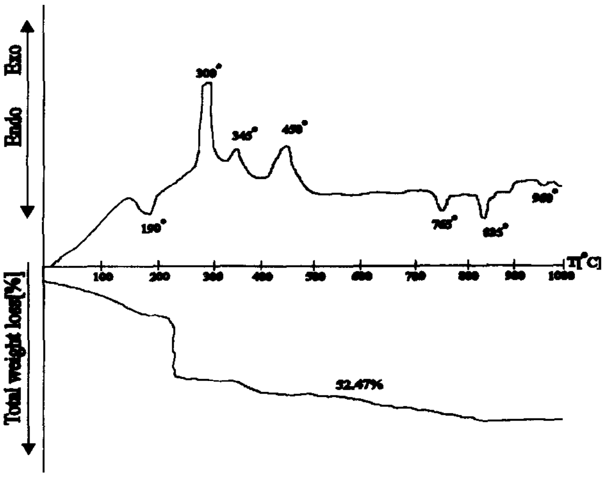


Fig. 5. DTA/TG curves for the four-components oxalates mixture.

The XRD patterns of the materials thermally treated at 600°C for 1 h are presented in Fig. 6.

At 600°C all oxalates are decomposed with the formation of oxides: CuO, Bi_2O_3 and carbonates $CaCO_3$, $SrCO_3$. $CuBi_2O_4$ and $SrBi_4O_7$ have also been identified.

The IR spectra of individual oxalates and multicomponent coprecipitates thermally treated at 600°C are shown in Fig. 7.

The characteristic bands for the oxalate group vanished from all the samples. The characteristic bands of the carbonate group in the case of Sr and Ca individual oxalates are evidenced at 1460–1400 (νas CO_3^{2-}), 1070 (νs CO_3^{2-}), 870–855 (δ CO_3^{2-} out of plane), 710–700 (δ CO_3^{2-}) cm^{-1}. In the case of the samples of Bi and Cu, individual oxalates are present with the specific bands of the M–O bond at 545, 500, 430 cm^{-1} (ν Bi–O) and 500 cm^{-1} (ν Cu–O).

Therefore, Ca and Sr oxalates form the corresponding carbonates and Cu and Bi form the corresponding oxides, in good agreement with XRD patterns observation.

The quaternary mixture was present in all the bands as observed in the case of individual samples.

In the range where the M–O band occurs some supplementary bands and shoulders were noticed. This can be correlated with the formation in the

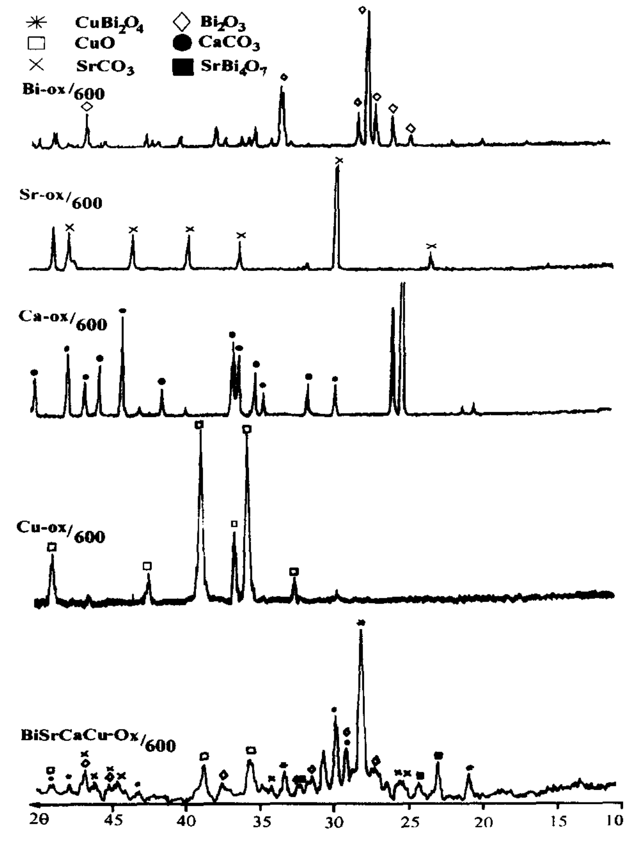


Fig. 6. XRD patterns of the individual oxalates and four-components oxalates mixture thermally treated at 600°C for 1 h.

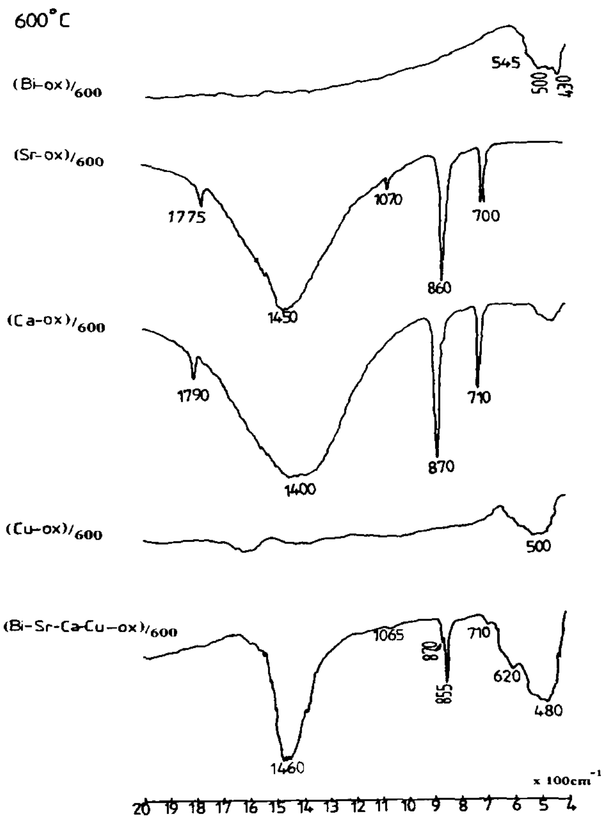


Fig. 7. The IR spectra of the individual oxalates and four-components oxalates mixture thermally treated at 600°C for 1 h.

last case of $CuBi_2O_4$ and $SrBi_4O_7$, which was also noticed in the XRD patterns.

After 1 h annealing at 600°C, as the results of the reaction processes mentioned above, the surface area of the powders decreased in the range of 5–7 m^2/g.

The powder morphology of the thermally treated precipitate at 600°C 1 h is shown in Fig. 8(a), (b). The shape and dimension of the initial crystals are changed and an agglomeration tendency is noticed. The size of the crystals is in the range of 0.3–1.5 μm and they have a booklet-like shape.

The TEM micrography results of the coprecipitates confirm the XRD and IR results.

According to the results presented above, by thermal treatment at 600°C the oxalates coprecipitation change to a mixture of crystallized oxides and carbonates.

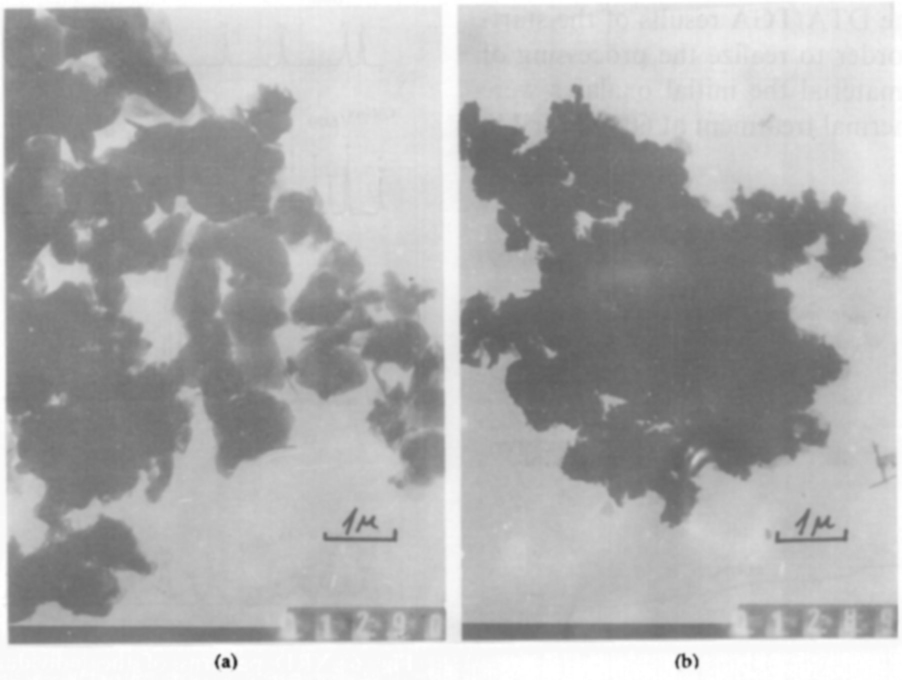
The reaction mechanism above this temperature is identical with that of the solid-state reaction mechanism. The difference mainly consists of a high reactivity of the precursor powders due to the submicron dimension as well as to the advanced homogeneity realized by coprecipitation.

The further thermal treatments have been realized according to DTA/TGA. The phase composition and the ceramic properties are shown in Tables 2 and 3.

The data presented in Table 2 show that at 750°C, the 2201 phase is formed besides unreacted CuO and $SrCO_3$. At 800°C, the 2201 conversion into 2212 phase started and the 2223 phase also begins to form. At 850°C, the 2201 phase is totally converted into the 2212 phase—which is also the major phase—and the 2223 phase is also noticed.

At these temperatures all the phases identified below 800°C are completely reacted to form the 2212 phase and a small amount of the 2223 phase.

In order to obtain pure 2223, high T_c superconducting phase supplementary prolonged thermal treatments are required.



(a) (b)

Fig. 8. TEM observation of BSCCO sample thermally treated at 600°C for 1 h.

Table 2. The results of XRD analysis of the samples thermally treated above 600°C

Sample	*Annealing treatment*		
2223	750°C/4 h	800°C/4 h	850°C/4 h
	2201,[a] $SrCO_3$, CuO	2201, 2212, 2223,[a] CuO	2212, 2223,[b] CuO

[a]Begin to form.
[b]Trace.

Table 3. Ceramic properties of the thermally treated samples

Temperature			
Property	750°C/4 h	800°C/4 h	850°C/4 h
Linear shrinkage (%)	6·00	7·85	4·68
Density (g/cm^3)	4·36	4·88	4·43
Porosity (%)	1·73	0·83	0·32

The ceramic properties of the samples thermally treated at 750, 800 and 850°C are presented in Table 3. For the samples thermally treated the densification reaches a maximum value at 800°C and a decrease at higher temperature. This fact can be explained by taking into account the formation of layered and bidimensional structure and their random orientation.

4 Conclusions

The oxalate route is one of the most promising chemical methods for the synthesis of high T_c superconducting materials.

Quantitative coprecipitation conditions were established.

Highly homogenous powders that consist of individual particles ranging in the nanometric domain have been obtained.

Compared to superconducting ceramic materials obtained by a classic route, the reactive oxalate powders allow the decrease of both thermal treatment periods and temperature, emphasizing a high microstructure homogeneity of the ceramic body.

In order to obtain pure 2223 high T_c superconducting phase, supplementary prolonged thermal treatments are required.

The high reactivity of the precursor powders obtained by the oxalate coprecipitation method lead to the obtaining of the superconducting phases at shorter times and at lower final temperatures of thermal treatments.

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