

Chelating agent effects in the synthesis of mesoscopic-size superconducting particles

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Abstract Several routes and procedures have been used in these last years as an effort to achieve single-phase mesoscopic-size superconducting samples. In this paper, the effects of using citric acid (CA), tartaric acid (TA) and ethylenediaminetetraacetic acid (EDTA) as chelating agents and ethylene-glycol (EG) as polyhydroxy alcohol were studied in order to establish conditions to avoid the occurrence of BaCO_3 undesirable secondary phase in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO). Thermal evolution of intermediate compounds formed during the calcinations process by the use of different chelating agents was traced using thermogravimetric and spectroscopic methods. The obtained results indicated that the polymer breakdown of samples prepared using EDTA occurs at higher temperatures than others chelating agents and also reduces the occurrence of BaCO_3 secondary phase as studied by X-ray diffraction measurements. Furthermore, the magnetic response of the mesoscopic-size YBCO specimens obtained was verified showing that samples present different superconducting response.

Keywords Polymeric precursors · Superconductors · Mesoscopic size materials

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1 Introduction

The synthesis procedures of high temperature superconducting materials (HTS) have been extensively studied in these years. Superconducting properties of ceramic superconductors are largely influenced by extrinsic characteristics that strongly depend on the sample preparation routes, as well as occasional subsequent processing [1].

Several problems are associated to the synthesis of YBCO superconducting phase, as presented by Kakihana [2], since temperatures used to achieve this desired phase is usually high, due to the formation of the barium carbonate (BaCO_3), which is stable up to a temperature of 815–850 °C. In such temperature, ceramics processes of the grain size growth are completely active, avoiding the occurrence of mesoscopic size specimens.

In order to avoid higher synthesis temperatures, chemical routes are the most appropriate approach to be used. Polymeric precursor methods consist in a polyesterification process of a metal chelate complex by using a hydroxycarboxylic acid and a polyhydroxy alcohol in an aqueous solution that is turned into a polymeric gel. A subsequent heat-treatment obtains an amorphous powder that is then calcined to achieve the desirable phase in aggregates of small crystallites.

In this paper, the $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) samples were synthesized by using a polymeric precursor method, known as the Pechini method [3]. Citric acid (CA), Tartaric acid (TA) and Ethylenediaminetetraacetic acid (EDTA) were used as chelating agents to study the influences of such compounds in the thermal and structural characteristics of the prepared specimens. The use of diverse chelating agents to the synthesis of another phase in YBCO family was already studied in order to obtain single-phase samples [4, 5]. It was found that the use of TA avoided the

occurrence of metallic acetates segregation during the synthesis, resulting in a high quality sample.

Otherwise, it is known that ethylenediaminetetraacetic acid (EDTA) has biggest ability to form stable solution and it having four carboxylic acid groups can react with ethylene glycol (EG) [2]. The citric acid (CA), commonly used in Pechini method, own three carboxylic acid groups and the tartaric acid (TA) has two -COOH and two -OH groups. The thermal evolution and effects of different chelating agents were studied in order to obtain the mesoscopic-size YBCO specimens at lower temperatures.

2 Experimental details

The samples were prepared from metallic ion containing aqueous solution, as shown in the flowchart of Fig. 1. Firstly, stoichiometric amounts of Y_2O_3 , BaCO_3 and CuO were dissolved into water by adding HNO_3 . These salts were mixed with the chelating agent, at the metal/chelating agent proportion of 1/3. The ethylene glycol was added at a temperature of 60°C , with a chelating agent/ethylene glycol mass ratio of 60/40 [6]. Under constant stirring, NH_4OH was added until the pH of the solution was 7. The temperature was increased up to 90°C in order to evaporate the water and form the gel.

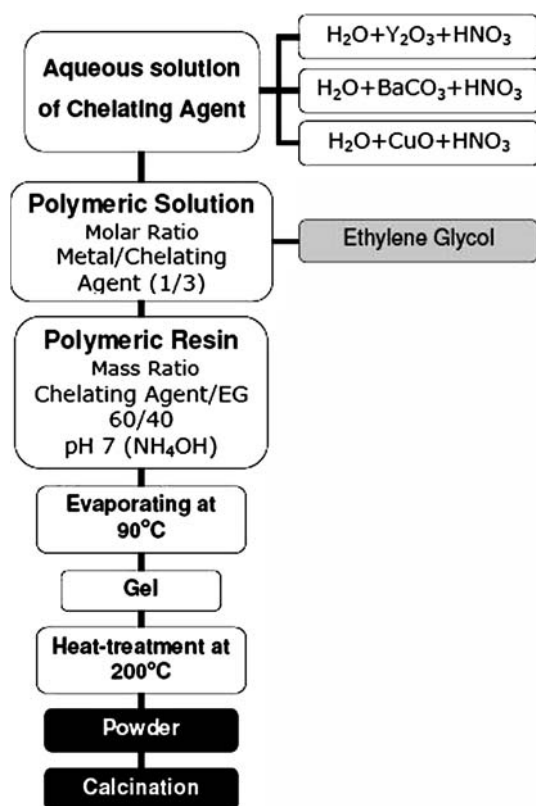


Fig. 1 Flowchart of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sample preparation

Effects of different hydroxycarboxylic acid were studied through Thermogravimetric studies (TG/DSC), Fourier Transform Infrared spectroscopy (FTIR), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Differences on the superconducting response of the powders were analyzed by magnetization measurement performed with a Quantum Design SQUID Magnetometer.

3 Results and discussion

In Fig. 2 it is shown the results of TG-DSC measurements performed in the samples, after a heat-treatment at 200°C , obtained from different chelating agents. As can be observed, the mass loss starts at around 100°C by the reduction of about 5–10% of weight, attributed to the adsorbed water evaporation (endothermic process). The major mass loss (around 80% of loss) occurs between 300 and 900°C which behavior is practically the same for all samples. Around 300°C the polymer breakdown occurs by

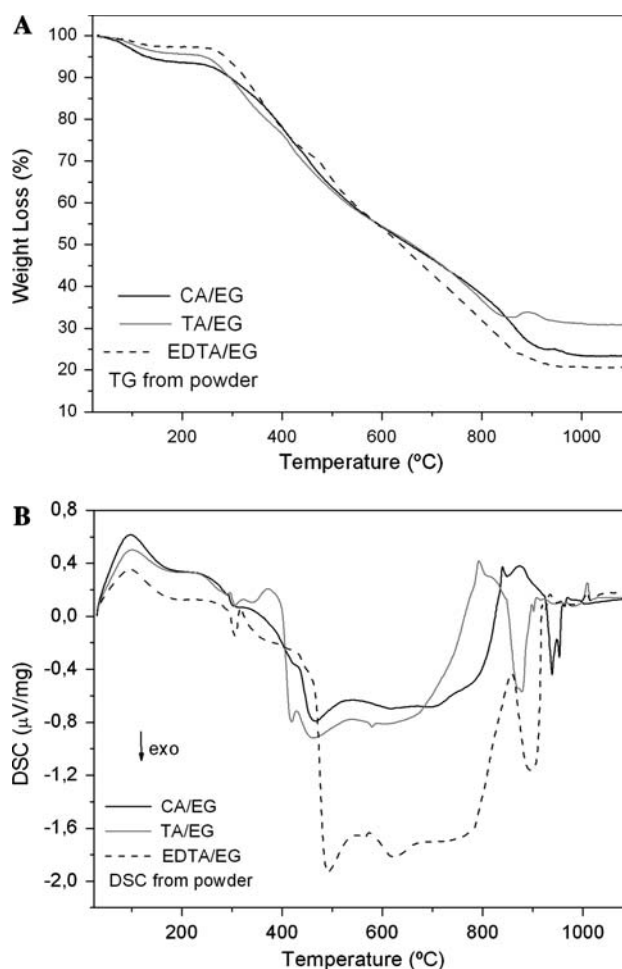


Fig. 2 Simultaneous thermal analysis performed in air on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ precursor powders obtained from the gel treated at 200°C for 30 min: (a) TG and (b) DSC

fragmentation and water and carbonic gas releasing [2]. This exothermic process represents 20–30% of total loss. After that the process corresponding to a big and wide DSC exothermic peak is observed, corresponding to the elimination of the organic material present in the samples, as seen in Table 1. These large peaks can overlap the endothermic processes as decomposition of carboxylic groups, carbonates and nitrates [7], originated from the polymer and nitric acid. The endothermic process between 800 and 900 °C refers mostly to the decomposition such as carbonate, which is followed by the exothermic process that can be attributed to the formation of superconductor stable phase. The remaining carbonates, probably of barium, decompose at the temperature higher than 850 °C, characterized by two endothermic peaks. It can be noted that the percentage of mass loss is greater for the sample with higher molecular weight indicating the elimination of a great part of the organic component takes place in the temperature higher than 200 °C, up to values of 800 °C. The DSC results show that the breakdown for the polymer prepared using EDTA as chelating agent occurs at higher temperatures than compared with CA and TA.

After examining thermal-analysis data, some samples were heat-treat in specific temperatures in order to perform FTIR measurements to study the structural transformations in these different temperatures. Some spectra were taken from the polymeric gels and samples treated at temperatures of 200, 400, 800, 850 and 900 °C, for 30 min (heating rate of 10 °C/min). Representative results are shown in Figs. 3–8. The spectra obtained from gels, shown in Fig. 3, present peaks centered in the following regions: 3,800–3,200, 3,200–2,800, 1,750–1,400, 1,300–830 and 800–400 cm^{-1} . The intense and wide band at 3,700–3,200 cm^{-1} is due to the symmetric and asymmetric stretch frequency of –OH group overlapped with stretching vibration of –CO–OH, vibrations of metal attached –OH group and its interactions, as hydrogen bridges, between water and alcohol molecules present in the gel structure, deriving from hydroxycarboxylic acids and EG [8, 9]. The bands 1,550–1,400 cm^{-1} and 1,000–830 cm^{-1} refer to –OH bending. At 3,200–2,800 cm^{-1} range refers to C–H symmetric and asymmetric vibrations of the –CH₃ and –CH₂– groups, and around 1,400 cm^{-1} due to C–H bending vibration [10]. The small band approximately at 2,350 cm^{-1} , which can be seen in all spectra presented hereinafter, refers to the carbon dioxide (CO₂) of atmosphere [7]. The very strong region

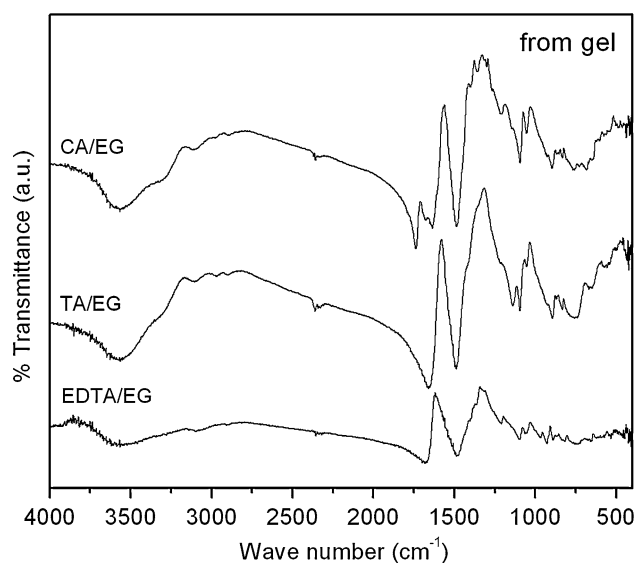


Fig. 3 FTIR spectra from the precursor gel

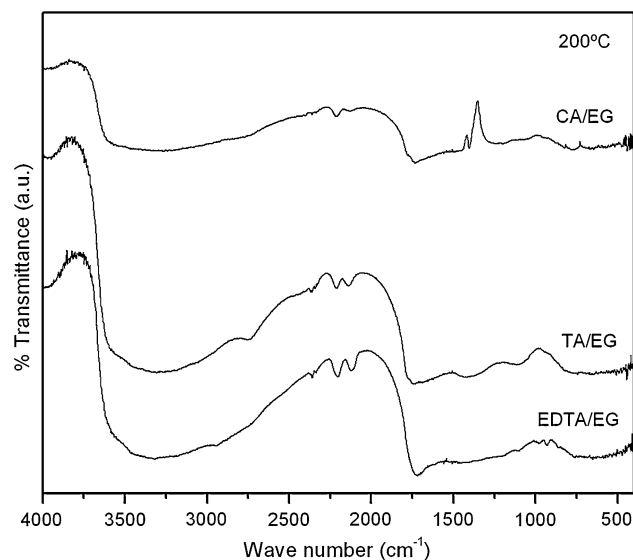


Fig. 4 FTIR spectra from the powder heat-treat at 200 °C

between 1,700 and 1,550 cm^{-1} refers to the stretching vibration of the –COO[–] groups with the metal ions [11]. The intense peak at 1,736 cm^{-1} as well as a band at 1,180–1,230 cm^{-1} when CA was used, indicating the occurrence of esterification [12] at 90 °C, temperature used for remove water to form gel. Another peaks to verify the esterification process efficient are at 1,338 and 1,093 cm^{-1} , referring to the presence of asymmetric stretching of =C–O–C and C–O–C groups [13]. The peaks between 1,300 and 1,200 cm^{-1} refer to stretching vibrations –CH–OH and NO₃[–] groups, so the small peak at approximately 1,350 cm^{-1} confirms the presence of the NO₃[–] [13], derived from nitric acid. The vibrations ranging from 800 to 400 cm^{-1} refer to the Metal–O.

Table 1 Temperatures of the exothermal peaks for each sample

| Samples | Start (°C) | Finish (°C) |
|---------|------------|-------------|
| CA/EG | 360 | 825 |
| TA/EG | 400 | 764 |
| EDTA/EG | 325 | 917 |

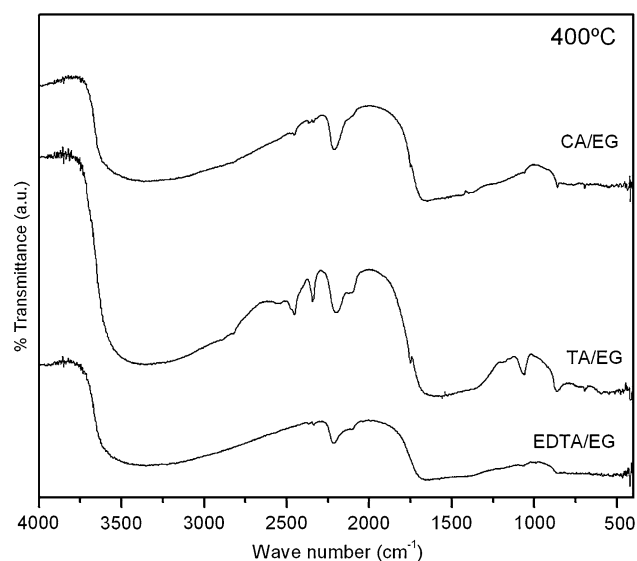


Fig. 5 FTIR spectra from the powder heat-treat at 400 °C

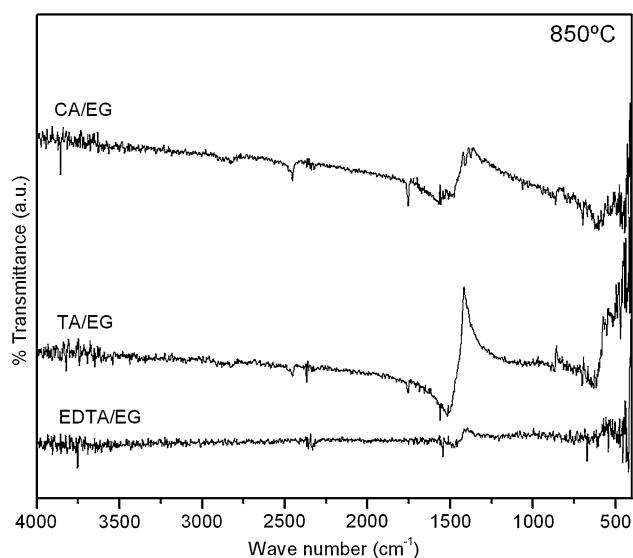


Fig. 7 FTIR spectra from the powder heat-treat at 850 °C

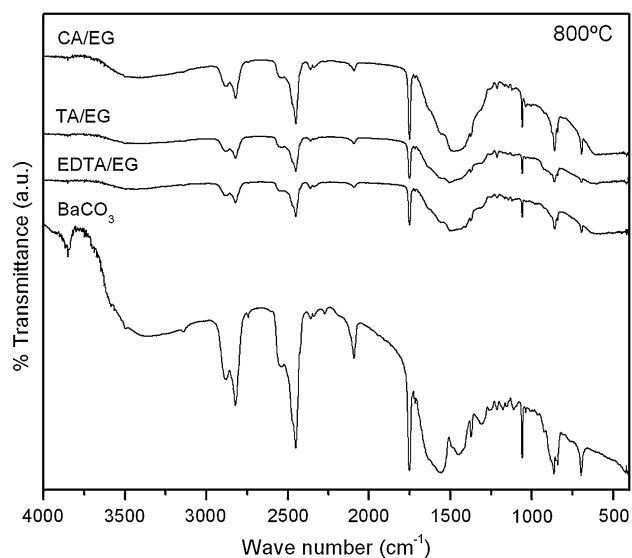


Fig. 6 FTIR spectra from the powder heat-treated at 800 °C and barium carbonate (for comparison)

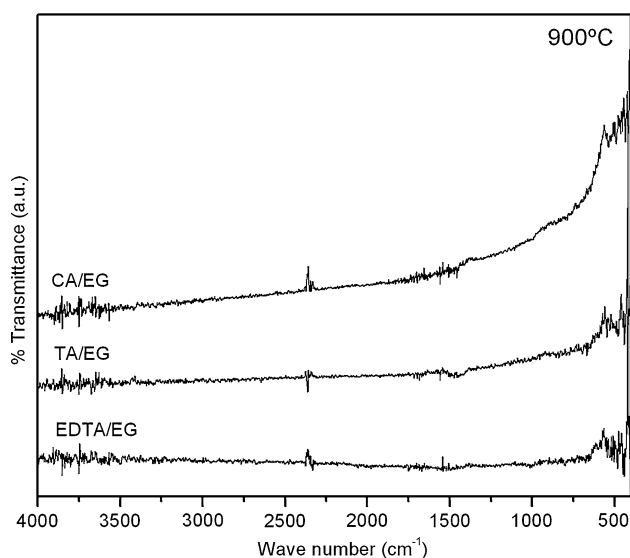


Fig. 8 FTIR spectra from the powder heat-treat at 900 °C

Obtained spectra from powder heat-treated in 200 and 400 °C can be observed in Figs. 4 and 5, respectively. It is possible to verify the bands in $3,800\text{--}3,200\text{ cm}^{-1}$ and $3,200\text{--}2,800\text{ cm}^{-1}$ that are more intense than of the gel due to higher concentrations of $-\text{CH}_3$ and $-\text{CH}_2-$, possibly because of the water evaporation. An average band in $2,300\text{--}2,000\text{ cm}^{-1}$ also arises, which can be attributed to the NH_3^+ group vibrations [14]. The result indicates that the main elimination of NH_3^+ containing groups takes place at a temperature higher than 400 °C. The peak of the ester group ($1,736\text{ cm}^{-1}$) vanish, and another bands refers to carbonate ions appeared at 860 and approximately $1,400\text{ cm}^{-1}$ [15] overlapping with stretching $\text{C}=\text{O}$. It is

clear even at 400 °C that the samples contain a great quantity of organic residues in their structure.

In Fig. 6 is presented the spectra for samples heat-treated at 800 °C showing the predominance of signal resulted by the interaction between barium carbonate (BaCO_3) and IR. For interpreting the spectra, we use a model consisting of CO_3^{2-} anions and Ba^{2+} cations isolated. The peak at 699 cm^{-1} referring to the bending in plane vibrations in CO_3^{2-} anion; peak at 856 cm^{-1} referring to the bending out of plane vibrations; peak at $1,060\text{ cm}^{-1}$ referring to the symmetric stretching vibrations; band at $1,500\text{--}1,400\text{ cm}^{-1}$ referring of the asymmetric stretching vibrations [16]. The formation of the BaCO_3 phase is undesired but it takes place due to the presence of

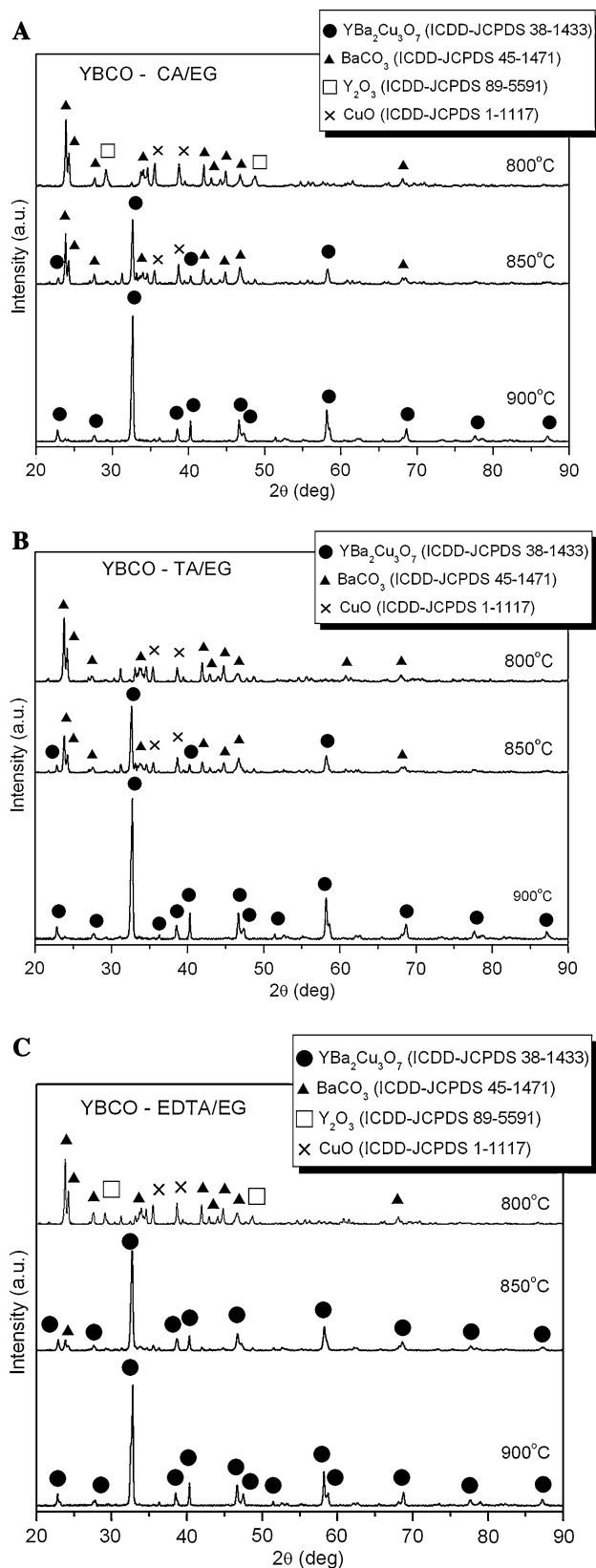


Fig. 9 XRD pattern for the YBCO samples prepared by using (a) CA, (b) TA and (c) EDTA

carboxylic group and the oxidation of barium bonded carboxylates produces BaCO_3 . During heat-treatments, the surface BaO can also react with atmospheric CO_2 forming the BaCO_3 [2] at temperatures of approximately 500°C [17], and it is decomposed at much higher temperatures. The kinetics of such decomposition is that determines the formation of the phase $\text{YBa}_2\text{Cu}_3\text{O}_y$ [18].

For samples heat-treated at higher temperatures, over 800°C , results indicates that BaCO_3 decomposes but still remains mainly in the case of CA and TA, which is characterized by the presence of the band at $1,550\text{--}1,350\text{ cm}^{-1}$ at 850°C , as shown in Fig. 7. In the synthesis using EDTA/EG, the remaining BaCO_3 is much less than that synthesis by using CA and TA, which indicates that the decomposition of this phase is more efficient or occurs at lower temperature than that with two other chelating agents or even the formation of BaCO_3 is not so favored. At 900°C , no quantitative differences were detected by the use of FTIR spectroscopy, as seen in Fig. 8.

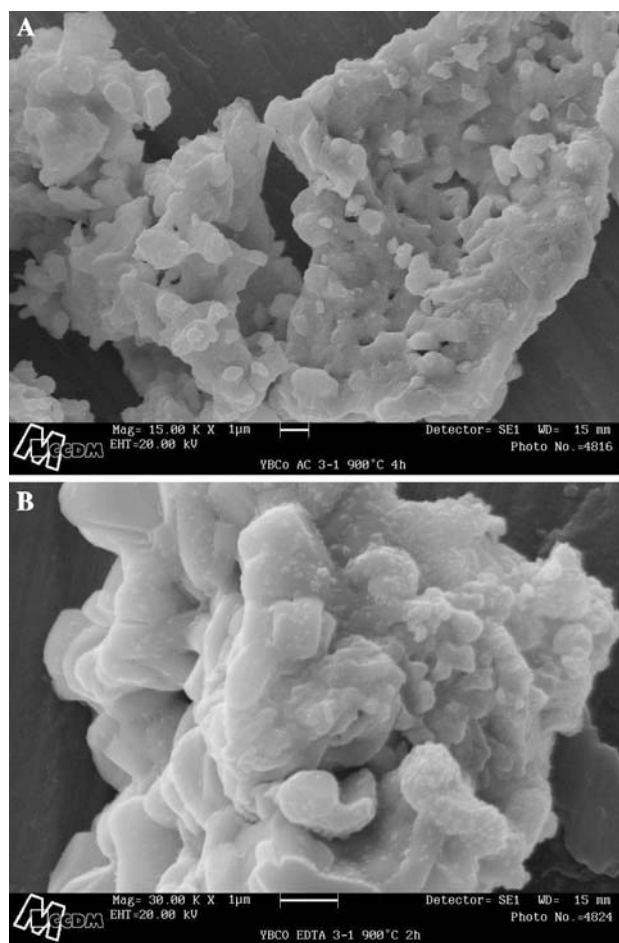


Fig. 10 Representative scanning electron images of YBCO prepared by (a) CA/EG and (b) EDTA/EG, both heat-treated at 900°C for 4 h

Table 2 Oxygen content for the different samples obtained by redox titration technique

| | CA/EG | TA/EG | EDTA/EG |
|-----------|-------|-------|---------|
| T_C (K) | 62 | 84 | 90 |
| y | 6.855 | 6.925 | 6.955 |

In order to verify the formation of the $YBa_2Cu_3O_{7-\delta}$ superconducting phase (ICDD-JCPDS 38-1433) and the presence of the secondary phase (barium carbonate, ICDD-JCPDS 11-697) in the prepared samples, X-ray diffraction (XRD) studies were performed. Figure 9 shows the diffractograms of the samples obtained using CA/EG, TA/EG and EDTA/EG and treated at temperatures of 800, 850 and 900 °C. As observed in the infrared spectra, the $BaCO_3$ is present as a main phase in the sample obtained by the three variations of preparation method and treated at 800 °C. Comparing the data for samples heat-treated at 850 °C, it can be seen that $BaCO_3$ and $YBa_2Cu_3O_y$ phases still coexist, with a smaller peak for the sample prepared by using EDTA.

By the use of the Debye–Scherrer equation [19] crystallite sizes were estimated and the results indicated 59 nm for the sample prepared with EDTA/EG, 44 nm for AC/EG and 44 nm for the one prepared using TA/EG. To illustrate morphology of some prepared specimens, SEM images of the EDTA/EG sample heat-treated at 900 °C can be seen in the Fig. 10.

Another important characteristic for ceramic superconducting materials is oxygen stoichiometry. This quantity indicates oxygen deficiency of calcined samples and reflects the effects of the heat-treatments in terms of the magnetic response of the prepared specimens. Table 2

shows the oxygen stoichiometry for the samples prepared using the different hydroxycarboxylic acids as chelating agents calcined in air at 900 °C for 30 min.

One can observe from Fig. 11 magnetization as a function of temperature measurements for all prepared samples heat-treated in air at 900 °C. It can be seen that all samples present superconducting response and the highest critical temperature (T_C), around 90 K, is present by the sample prepared with EDTA. This behavior could be related to the fact of EDTA is a better chelating agent eliminating $BaCO_3$ phase at higher temperatures and allowing a better oxygen stoichiometry. Otherwise, the sample CA/EG presented T_C around 62 K, the lowest among the prepared samples.

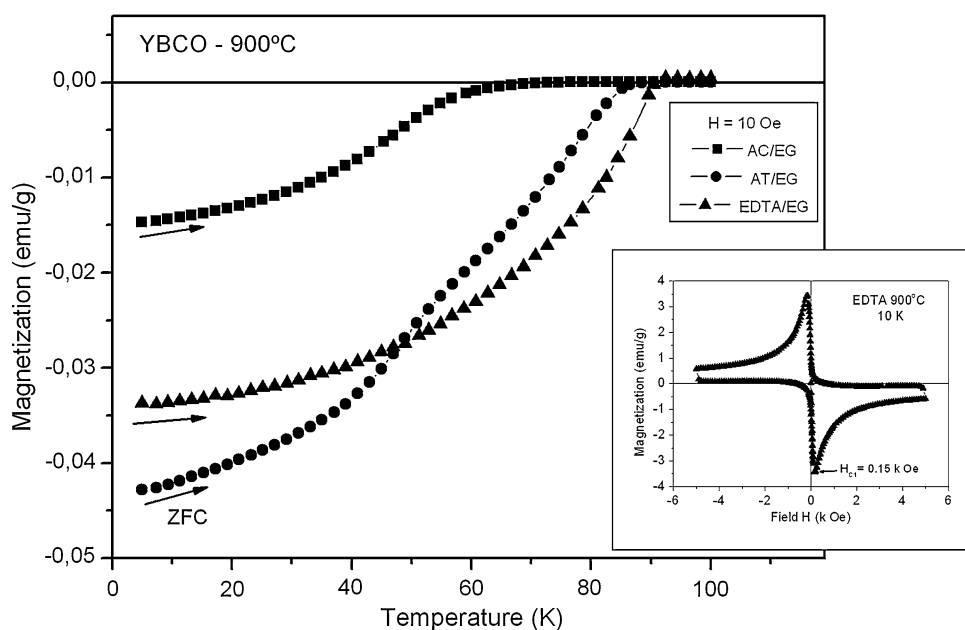
4 Conclusions

Several different procedures have been used to produce superconducting samples in small scales in these last years, but there are still several open questions related to the chemistry of such processes.

In this study results indicate that the use of EDTA as chelating agent prevents of the occurrence of $BaCO_3$ secondary phase at lower temperatures as indicated by XRD analyses. Otherwise, DSC data showed that the polymer breakdown occurs at higher temperatures than others chelating agents.

At 400 °C the FTIR spectrum shows that the peak correspondent to the ester group at $1,736\text{ cm}^{-1}$ vanishes and another bands refers to carbonate ions appeared at 860 and approximately $1,400\text{ cm}^{-1}$ that corresponds to C=O bands.

Fig. 11 Magnetization as a function of temperature measurements for an applied magnetic field of 10 Oe for samples prepared using different chelating agents. Inset shows magnetization versus applied magnetic field for EDTA/EG sample



It was also found that for samples heat-treated at higher temperatures, the results indicate that BaCO₃ still remains mainly for samples prepared using CA and TA as chelating agents.

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