

OPTIMIZATION OF THE SINTERING PROCESS BY DSC FOR THE PREPARATION OF HIGH-TEMPERATURE SUPERCONDUCTORS

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Abstract

The optimum calcination and sintering conditions for the preparation of the desired phases with the proper stoichiometry of the bulk high-temperature superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (BSCCO) were investigated by differential scanning calorimetry. DSC analysis on the corresponding superconducting coatings, electrophoretically deposited, indicated that the sintering and annealing procedure was suitable for the production of stable, strong and adherent coatings. X-ray diffraction analysis, Raman spectroscopy and magnetic measurements confirmed the improved properties of the superconducting powders and coatings obtained.

Keywords: $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, DSC, electrophoretically deposited superconducting coatings, high-temperature superconductors, magnetic measurements, Raman spectroscopy, X-ray diffraction, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

Introduction

As high-temperature superconductors (HTS) are currently of great interest in technology, control of their production and processing is becoming ever more important. During the preparation of HTS bulk materials and their coatings by multistage processes [1], optimized heat treatment is required, in order to attain the proper stoichiometry and homogeneity of the superconducting powders and the optimum adhesion and density for the coatings. Thermoanalytical techniques are the most suitable methods to follow the phase transitions and their corresponding temperatures, especially in the calcination and sintering of HTS [2]. Among the different HTS, the yttrium-barium-copper oxide high- T_c superconductor ($\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, $x=0.0-0.2$, YBCO 123) and bismuth-strontium-calcium-copper oxide ($\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ $n=1,2,3$ BSCCO) are perhaps the most important, due to their technological applications, and their process routes, phase formations and thermodynamic stabilities have been investigated by means of

thermal analysis [2–8]. However, numerous problems arise in consequence of the complexity of the process, and the preparation of pure powders and coatings from these HTS requires careful study. In the present investigation, the calcination and sintering conditions for the preparation of YBCO 123 powders by the solid-state reaction and by oxalate coprecipitation, together with the sintering procedure on the electrophoretically deposited YBCO coatings produced [9, 10] were optimized by means of DSC. Through this technique, the conditions for the production of BSCCO (2212) superconducting powder by the solid-state reaction were optimized. The DSC results were verified by X-ray diffraction analysis and micro-Raman spectroscopy, while the superconducting properties were tested by magnetization measurements with a superconducting quantum interference device (SQUID).

Experimental

Reagents

All reagents used were of analytical grade: Y_2O_3 , purity 99.99% (Alfa Johnson Matthey), $BaCO_3$, purity >99% (Merck), CuO , purity >99% (Merck), $Y(NO_3)_3 \cdot 6H_2O$, purity >99.9% (Alfa Johnson Matthey), $Ba(NO_3)_2$, purity >99% (Carlo Erba), $Cu(C_2H_3O_2)_2 \cdot H_2O$ p.a. (Merck), $(COOH)_2 \cdot 2H_2O$ purity >98% (Carlo Erba), Bi_2O_3 , purity >99.9% (Aldrich Chem. Co.), $CaCO_3$ purity 99.5% (Carlo Erba), $SrCO_3$, purity >99% (Johnson Matthey) and oxygen, purity 99.999% (Air Liquid).

As substrates for the coatings, Au/Si-wafers, silver sheets and plates (1–15 cm²) were used. The organic solvents applied for the electrophoretic deposition of YBCO were 1-butanol (Merck) and 1-propanol (Ferak).

Apparatus and instrumentation

The calcination and sintering of the superconducting powders and the coatings were carried out in a tube furnace (Thermawatt, max. temp. 1050°C, i.d. 5 cm) equipped with an automatic temperature controller (9 steps) and a gas inlet for the oxygen flow.

The electrophoretic deposition of the finely ground superconducting powder, suspended in the organic solvent, was performed in a temperature-controlled glass cell, described in detail elsewhere [9, 10]. The electric field between the cathode (the corresponding substrate for the coatings) and the anode (an Ag sheet) was produced by a power supply (CONSORT E734), max. voltage 3000 V and max. current 99.99 mA).

The differential scanning calorimeter was the mod. HT 1500 Stanton Redcroft (fin. temp. 1500°C, with programmable heating-cooling rate).

The X-ray diffraction analysis was performed with a Siemens diffractometer (D5000), using $CuK_{\alpha 1}$ radiation with a graphite monochromator, in the 2 theta

range from 10 to 60 degrees. The power conditions were set at 20 kV/30 mA. The patterns were evaluated by the DIFFRAC. A. T. Search Program supplied by Siemens. The experimental data were compared with the corresponding JCPDS files.

For the measurements by micro-Raman spectroscopy, a Jobin-Yvon T 64000 Raman spectrometer (Ar⁺-laser, 514.5 nm, 0.1–0.2 mW) coupled to an Olympus metallographic microscope was used.

The temperature dependence of the magnetic susceptibility was measured with a Quantum Design (USA) Magnetic Property Measurement System (MPMS), Mod. 1822) equipped with a SQUID amplifier and a He cryogenic system. The samples were cooled in different magnetic fields (0.002–0.02 T) from 100 K down to 5 K (field cooled measurement), measurements being made every 5 K.

Analytical procedure

For the preparation of the YBa₂Cu₃O_{7-x} powders, the solid state reaction and oxalate coprecipitation techniques were used, while the preparation of the superconductor Bi₂Sr₂CaCu₂O_y was based on the solid-state reaction method.

Powders of Y₂O₃, BaCO₃ and CuO were finely ground and well mixed in a mole ratio of 1:4:6 in order to achieve the proper stoichiometry of 1:2:3 for YBCO (123). The resulting mixture was pressed into pellets and subjected to a calcination, sintering and annealing process, following the thermal cycle shown in Fig. 1 (curve I).

In particular, the mixture was heated under an oxygen flow (1 cm³ min⁻¹) at a heating rate of 10 °C min⁻¹ up to 960°C, where it was kept for 12 h. Afterwards, the temperature was decreased to 540°C (10°C min⁻¹), the bulk material being kept at this temperature for annealing for 12 h under an oxygen flow.

In the coprecipitation method, yttrium nitrate, barium nitrate and copper acetate were dissolved in water in a stoichiometric ratio near to 1:2:3, with the barium and copper in a small excess. This solution was reacted with the appropriate 0.5 M oxalic acid solution in 10% mole excess and the pH was adjusted to 4.5 by adding dilute ammonia. The light-blue precipitate was centrifuged and dried at 90°C for 1 h. The final dry powder was inserted into a tube furnace, calcined at 520°C for 1 h in air, and afterwards sintered at 910°C for 3 h, as shown in Fig. 1 (curve II) [11]. The thermal conditions for the annealing process were the same as for the solid-state reaction.

For the preparation of the BSCCO (2212) superconducting powder, Bi₂O₃, SrCO₃, CaCO₃ and CuO were mixed in appropriate amount with a Bi:Sr:Ca:Cu cation ratio of 2:2:1:2 and finely ground. The resulting mixture was heated for 96 h at 805°C under air, with two intermediate grindings.

The different stages in the above-mentioned various thermal cycles of the bulk materials, were estimated in advance by DSC measurements under air, with

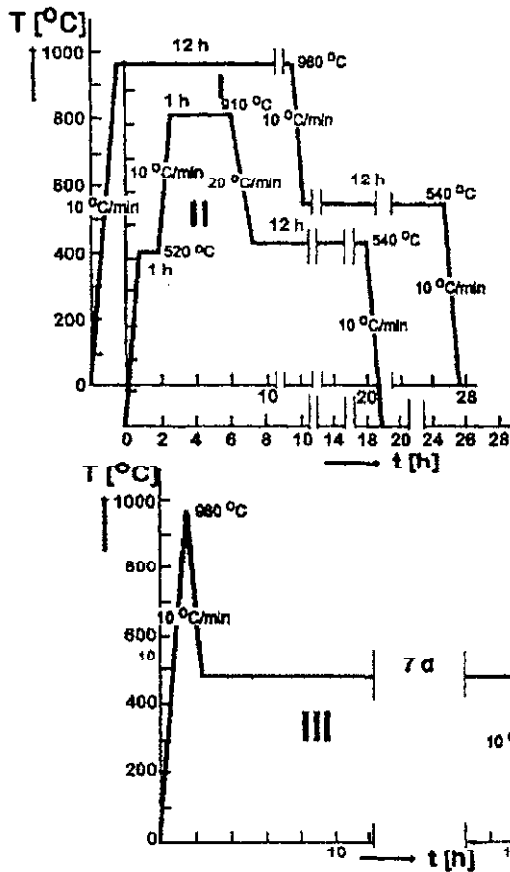


Fig. 1 Calcination and sintering process for the production of YBCO powder and coating;
I. Solid-state reaction; II. Oxalate coprecipitation; III. Sintering of YBCO coating

Al_2O_3 as reference material. The sample mass in all DSC measurements was 100 mg and the heating rate was $10\text{ C}^\circ\text{ min}^{-1}$.

Production of YBCO coatings

After the preparation of the bulk YBCO powder, a colloidal suspension was produced by vigorously mixing the bulk material with a mixture of organic solvents (butanol propanol 1:4) in a concentration of 1.5 g/100 ml in the electrophoretic cell. After a sedimentation time of 30 min, in which the heavier particles were separated from the lighter ones, a voltage of 800 V was applied between the two electrodes and a superconducting coating was formed on the cathode (which was the substrate). The superconducting coatings with a thickness of 10–15 μ that were produced within 5–10 min were dried at 150°C for 30 min to remove

the organic solvents and afterwards sintered at 960°C for 3 min. The annealing process on the coatings was performed at 470°C for 7–10 days under an oxygen flow (Fig. 1, curve III). The thermal treatment of the coatings was also estimated in advance by means of DSC measurements. The coatings produced were characterized for oxygen stoichiometry and superconducting phases by X-ray diffraction, micro-Raman spectroscopy and magnetization measurements.

Results and discussion

The thermal cycles to which the YBCO powders and coatings were subjected and determined by means of DSC measurements. Figure 2 presents the DSC curves obtained for the heat treatment of the precursors for the preparation of

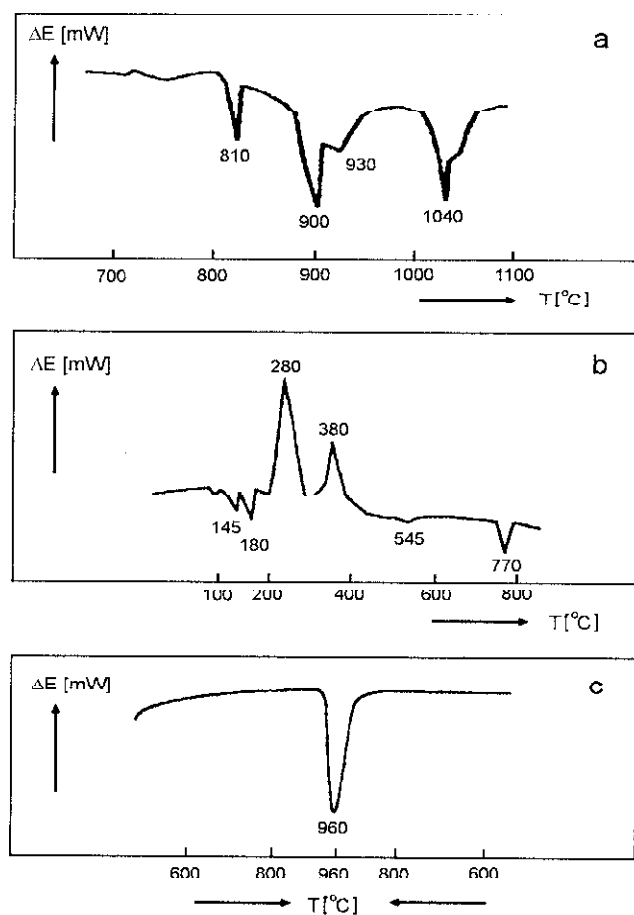


Fig. 2 DSC measurements on the raw materials of YBCO; a: solid-state reaction; b: coprecipitation method; c: DSC measurements on YBCO coatings

YBCO powders by the solid-state reaction (Fig. 2a) and oxalate coprecipitation method (Fig. 2b), and also the DSC curve obtained for the YBCO coating (Fig. 2c).

In Fig. 2a, in the temperature range 20–1080°C, the first endothermic peak, at 810°C, can be attributed to the decomposition of BaCO_3 . The second endothermic peak reflects the formation of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ from the intermediate phases BaCuO_2 , Y_2BaCuO_5 and $\text{Y}_2\text{Cu}_2\text{O}_5$. At 930°C (third endothermic peak), $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is formed in the reaction of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ with O_2 . Finally, at 1040°C, the decomposition and melting of YBCO occur [1, 2, 7, 8].

Figure 2b depicts the DSC diagram of the Y–Ba–Cu oxalate precipitate. In the temperature range 145–180°C, the loss of crystallization water occurs, followed by decomposition of the oxalate salts to their corresponding carbonates and oxides between 280 and 380°C [12]. The decomposition of BaCO_3 to BaO takes place at a lower temperature (770°C) than in the solid-reaction (790–810°C).

The great advantage of the production of YBCO by the coprecipitation method is that the average grain size obtained is smaller (1 μm) than the size of

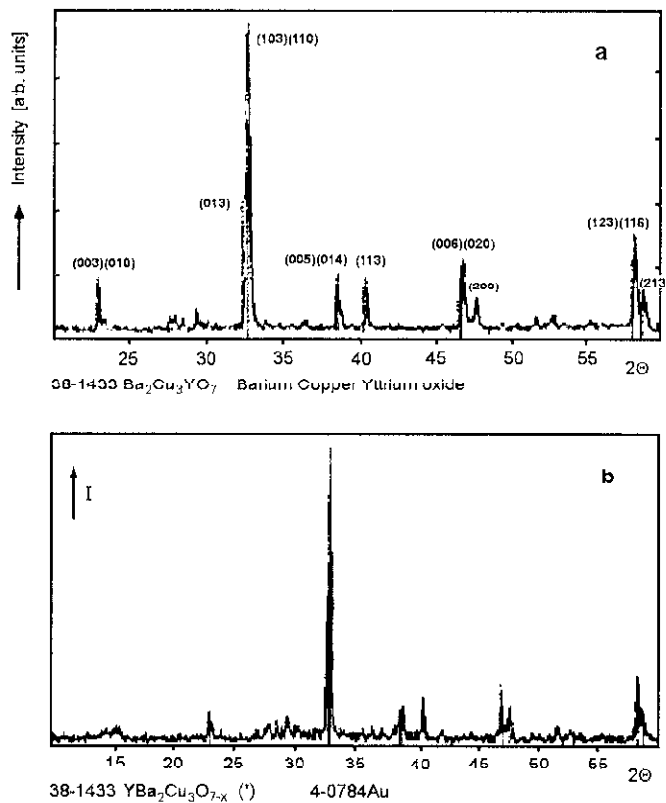


Fig. 3 XRD patterns of YBCO bulk material (a); XRD patterns of YBCO coating (b)

the grains produced by the solid-state reaction (5 μm). For this reason, the required sintering temperature of YBCO and the duration of the sintering process are smaller as compared with the solid-state reaction method (Fig. 1, curves I and II).

Figure 2c shows the DSC diagram of the YBCO coating. It can be observed that the only reaction which takes place is the partial melting of the grains of the coating at 960°C [10]. This measurement indicates that the coating has to remain during thermal treatment at 960°C for 3 min, so that adherence between substrate and coating is achieved through partial melting and single-crystal behaviour results. The coating subsequently remains at 470°C for 7 days under an O₂ flow for recovery of the lost oxygen and hence the superconducting properties.

The presence of the orthorhombic phase YBa₂Cu₃O_{7-x} ($x=0.0-0.2$) is proof of the existence of superconductivity. This YBCO phase could be verified in the produced bulk material and coating by X-ray diffraction analysis and Raman spectroscopy.

In the X-ray diffraction patterns of the bulk material and of the coatings (Fig. 3a, 3b), the peaks correspond to the YBa₂Cu₃O₇ orthorhombic phase (No. 38-1433 JCPDS pattern, International Center for Diffraction Data, USA). The only difference between the two patterns is the presence of Au (No. 4-0784 JCPDS pattern) in the spectrum of the coating due to its thinness.

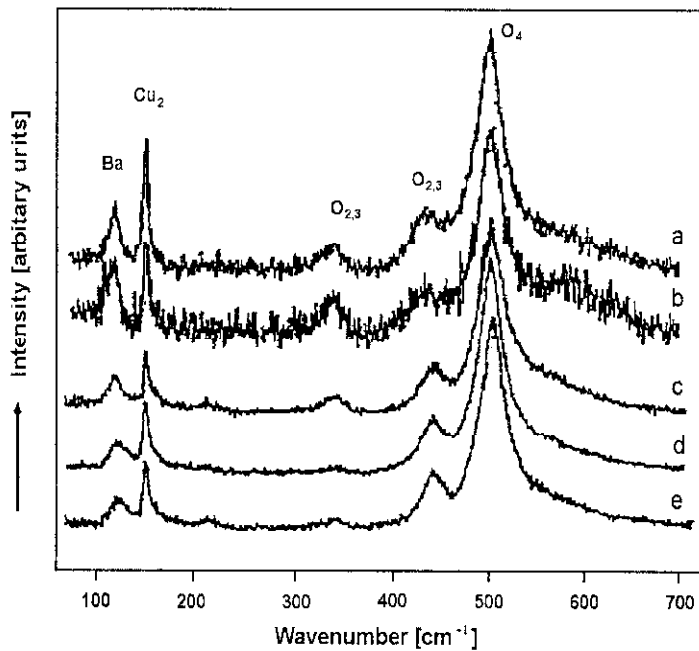


Fig. 4 Raman spectra of YBCO bulk material (a, b) and coating (c, d, e)

The non-existence of other phases and the homogeneity of the produced YBCO powders and coatings were also proven by micro-Raman spectroscopy measurements. This technique is very sensitive to stoichiometry changes, espe-

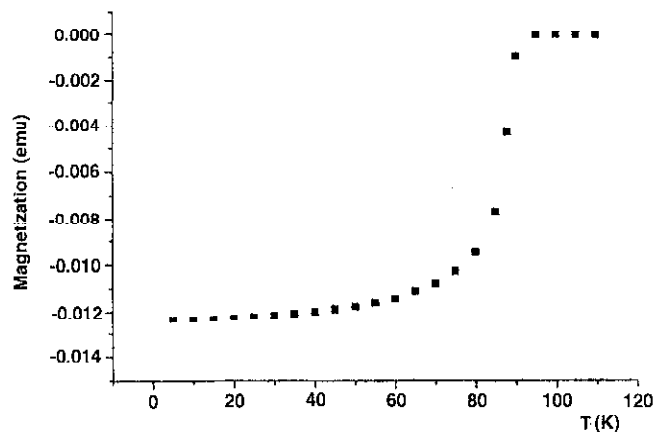


Fig. 5 Magnetization measurements vs. temperature for an YBCO coating on Si/Au substrate at 0.02 T

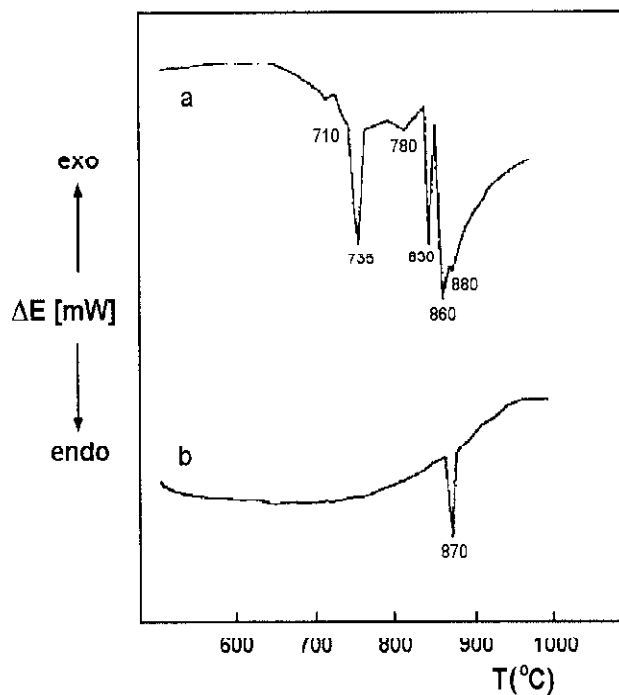


Fig. 6 DSC measurements on the raw materials of BSCCO: solid-state reaction (a); DSC measurements on BSCCO after reaction for 96 h at 805°C (b)

cially as concerns the oxygen content, and it can reveal the presence of undesirable dielectric phases in very small concentrations, and also the orientation of the grains in the films. As regards the Raman spectra of YBCO (Fig. 4), curves a and b refer to the bulk material and curves c, d and e refer to the coating. The

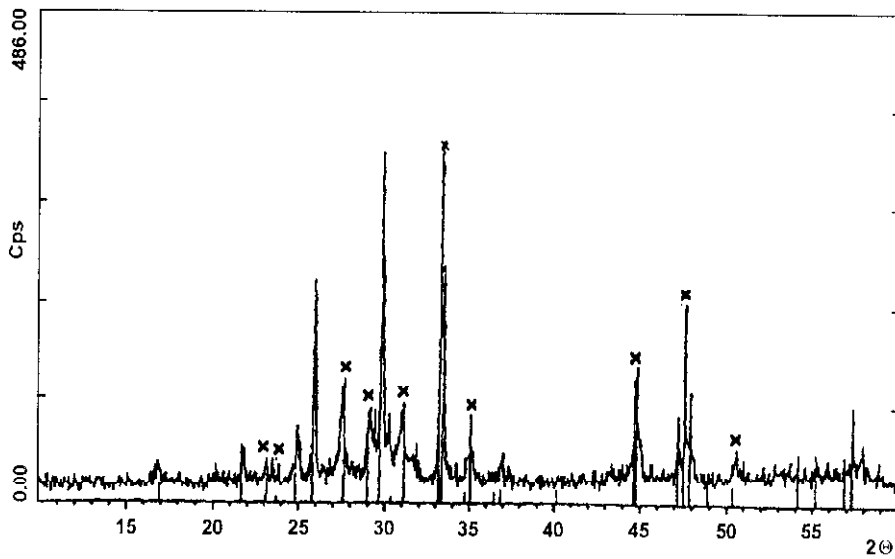


Fig. 7 XRD patterns of BSCCO after reaction for 96 h at 805°C. The indexed peaks correspond to the BSCCO 2212 phase, and the non-indexed peaks to the BSCCO 2201 phase

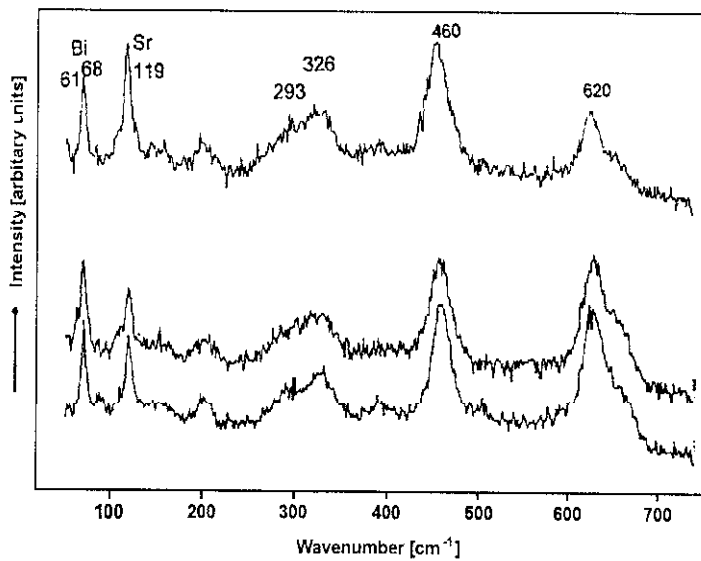


Fig. 8 Raman spectra of BSCCO after reaction for 96 h at 805°C

wavenumbers of the observed peaks, 116 cm^{-1} Ba zz, 148 cm^{-1} Cu₂ zz, 339 cm^{-1} O_{2,3} xx, 433 cm^{-1} O_{2,3} zz, 499 cm^{-1} O₄ zz (zz and xx vibrations in the z and x axis, respectively) correspond to the characteristic Raman frequencies of the five typical phonons of YBa₂Cu₃O_{7-x} [13]. Calibration graphs obtained with standard YBCO samples with different oxygen stoichiometries indicated an oxygenation degree of 6.9; no undesirable phases were obtained and the spectra were nearly identical in the different positions of the bulk material and coating, showing their homogeneity.

The magnetization measurements vs. temperature for the produced YBCO coatings furnished narrow transition curves with a critical temperature of $T_c=91\text{ K}$ and $\Delta T_c=2\text{ K}$ (Fig. 5), showing the high quality of the superconducting coatings produced after the sintering and annealing process. For the production of BSCCO (2212) as a bulk material by the solid-state reaction, the DSC measurement (Fig. 6a, temperature range 20–950°C) of the mixture of raw materials Bi₂O₃, SrCO₃, CaCO₃ and CuO reveals the decomposition of the carbonates in the range 710–780°C. The peak at 830°C corresponds to the melting of Bi₂O₃ [6]. The occurrence of the endothermic peaks in the range 860–880°C is probably associated with the formation of a liquid phase due to the melting of the Bi₂Sr₂CaCu₂O_y (2212) phase [15]. On the basis of these data, several trials were carried out in the range 790–820°C (step 2°C) in order to establish the optimum calcination temperature for BSCCO 2212, the mixture of raw materials exhibiting the best thermal behaviour at 805–810°C. Another factor which is very important for the calcination of BSCCO is the optimum reaction time for completion of the solid-state reaction of the 2212 phase. It was found that a reaction time of 96 h is adequate for the production of the superconducting powder, since only melting of the substance at 870°C occurs (Fig. 6b).

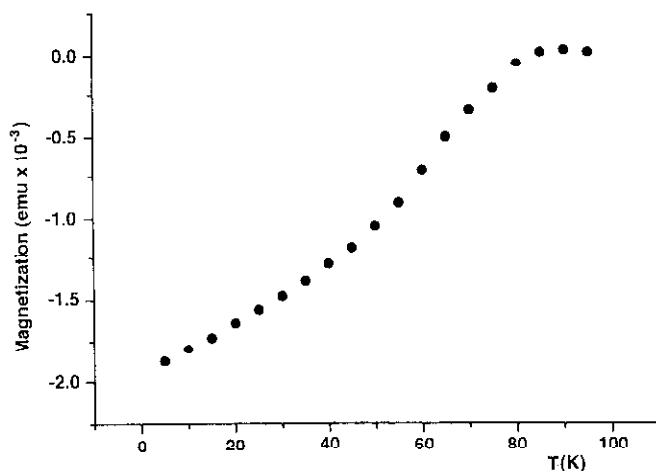


Fig. 9 Magnetization measurements vs. temperature on BSCCO powder at 0.002 T

Thus, it was concluded that a 96 h reaction at 805°C, prior to the melting point of Bi₂O₃, with 2 intermediate grindings (at 24 and 48 h, respectively) of the sample is sufficient for the production of BSCCO (2212) powder. The above results were verified by means of X-ray diffraction measurements (Fig. 7) and the Raman spectra (Fig. 8).

The XRD patterns reveal the presence of the phase Bi-2212 (Bi₂Sr₂CaCu₂O_y, No. 45-1058 JCPDS pattern) with the coexistence of the Bi-2201 phase (Bi₂Sr₂CuO_x, No. 39-0283 JCPDS pattern) in a small percentage (<10%). In the Raman spectra obtained on different grains of the BSCCO powder calcined at 805°C for 96 h, the peaks at 61, 119, 293, 460 and 620 cm⁻¹ are typical of the Bi-2212 phase [14], while those at 68 and 326 cm⁻¹ correspond to the Bi-2201 phase. Accordingly, it was concluded that in the produced BSCCO powder the main phase is Bi-2212 with the coexistence of Bi-2201.

The magnetic measurements demonstrated that the critical temperature of the bulk BSCCO powder was $T_c=85$ K (Fig. 9), which approaches the optimum value for the Bi-2212 phase [6].

Conclusions

DSC proved to be a useful technique for optimization of the calcination and sintering process, for the preparation of high-quality powders and coatings of the high-temperature superconductor YBa₂Cu₃O_{7-x} (YBCO 123) and for the preparation of Bi₂Sr₂CaCu₂O_x (BSCCO 2212) bulk material.

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