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Optimization of critical current density of bulk YBCO superconductor prepared by coprecipitation in oxalic acid

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$YBa_2Cu_3O_{7-x}$(YBCO) superconductor powder was prepared from mixtures of solutions containing yttrium, barium, and copper nitrates by coprecipitation in oxalic acid. Single-phase YBCO was obtained from a solution mixture of 14 vol% excess of barium nitrate and 12 vol% excess of copper nitrate relative to the stoichiometry of YBCO. The optimal pH in the coprecipitation process was determined to be 6.6–6.7 which was obtained by using 12 vol% excess oxalic acid anhydrous solution of the required oxalic acid to convert all metal cations to oxalates and adding a dilute ammonium hydroxide solution. The measurement of critical current density, J_c, of bulk YBCO prepared by the coprecipitation, showed a trend that the J_c increased together with the degree of orthorhombic distortion of YBCO phase which depended on the sample density and the content of impurity phases.

1. Introduction

A variety of applications of bulk high-temperature superconductors has been hampered by low transport critical current density, J_c, and sensitivity to weak magnetic fields due to the weak-link coupling between grains [1–4]. Because the parameters considered to weaken the intergranular coupling include porosity [5], microcracks [6], and impurities at grain boundary [7], the J_c of the bulk ceramic high-temperature superconductors is likely to depend upon sample density, grain size, and volume fraction of the superconducting phase. Indeed, it is known that an optimum J_c of bulk $YBa_2Cu_3O_{7-x}$(YBCO) superconductor is obtained from samples of an intermediate density [5, 8, 9], a fine grain size [8, 10], and an absence of the commonly observed non-superconducting phases such as Y_2BaCuO_5, $BaCuO_2$, $Y_2Cu_2O_5$, and CuO [11, 12]. The optimization of these material properties to achieve high J_c is expected to be determined by starting YBCO powders. In this context, comparative studies of YBCO powder synthesis methods [13–16] suggest that the solution-derived powders with a narrow distribution of particle sizes and a homogeneity of composition are attributed to high J_c of YBCO samples. These properties are governed primarily by the YBCO powder processing parameters such as starting chemicals and calcination temperature and atmosphere.

Previously, we have compared the J_c of bulk YBCO prepared from various powder processing routes, namely solid-state reaction, citrates route, and coprecipitation in oxalic acid [17]. Among them, the YBCO synthesized from the coprecipitation method showed superior superconducting properties. Nevertheless, the oxalate coprecipitation method involves difficulties for a complete precipitation of all components, difficulties which are closely related to the control of pH in the coprecipitation process [18, 19]. The pH of the oxalate coprecipitation process is affected by the amount and type of precipitants, titrating solutions, and starting chemicals. The purpose of the present study was to manipulate these processing parameters to optimize the J_c of bulk YBCO superconductor.

2. Experimental procedure

The starting chemicals for YBCO were $Y(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$, and $Cu(NO_3) \cdot 5/2H_2O$. Each of the nitrates was dissolved separately in deionized high-purity water to form 0.2 M solutions and then combined in various ratios to obtain the stoichiometry of YBCO after calcination. The coprecipitation was performed by pouring the solution into 1 M oxalic acid solution (of excess amount relative to that required to convert all metal cations to the oxalates) which was vigorously stirred. The oxalic acid anhydrous and the oxalic acid dihydrate were used as precipitants. The pH of the coprecipitation was varied by adding different amounts of dilute ammonium hydroxide solution which consists of 40 vol% ammonium hydroxide and 60 vol% deionized water. The precipitate was allowed to stand overnight and then centrifuged. The resulting precipitate was washed with deionized water and recentrifuged. After the second centrifuging, the precipitate was dried at 90 °C for 20 h in a vacuum oven. The pale blue agglomerates were broken by alumina mortar and pestle before calcination.

Initially, the dried powders were heated at 600 °C for 5 h in air, then were further calcined at 820 °C for 1 h, and then furnace cooled in 10 mm Hg flowing air. The resulting powders of about 15 g batches were ground by alumina mortar and pestle to pass the 325 mesh sieve. Specimens of a cylindrical shape (4 mm diameter and 20 mm long) were prepared by isostatically pressing the powders under 340 MPa. The pellets were sintered at temperatures ranging from 900–950 °C for various times and annealed at 450 °C for 5 h during cooling in flowing oxygen. The phases in the calcined powders and the sintered samples were examined by X-ray diffraction (XRD) with CuK_α radiation. The density was determined by measuring dimensions and weight of sintered specimens. J_c was measured by a d.c. four-probe method with the 1.0 μV cm^{-1} electric field criterion in liquid nitrogen. Indium solder was attached as a contact.

3. Results and discussion

For the preparation of YBCO single phase it is a common practice to add excess amounts of barium and copper nitrates [18, 20] to alleviate the problems concerning the oxalate coprecipitation method, that is, the solubility of the barium salt at low pH and the complexation of copper in the presence of excess oxalate [21]. In the previous study [17], a 100 ml Y^{3+}: 228 ml Ba^{2+} : 335 ml Cu^{2+} nitrates solution ratio rendered a good-quality YBCO powder by coprecipitation in an essentially neutral solution, i.e. a pH near 7, which gives a very low ionic strength [22]. Thus the ratio was fixed throughout the present investigation.

XRD patterns for as-dried powder after coprecipitation and powders calcined at different temperatures are shown in Fig. 1. The complex XRD pattern of as-dried powder indicates that the precipitated powder contains several phases. Horowitz *et al.* [16] have reported that the powders prepared by the coprecipitation were a mixture of the barium nitrate, copper oxalate, and an unidentified phase. In addition to the nitrate and the oxalate, yttrium nitrate and barium oxalate were identified, whose main peaks are positioned at 2θ of 16.1 ° and 24.7 °, respectively, in Fig. 1. Thus the dried precipitate was composed of oxalates and nitrates of the constituent metal cations. The XRD pattern of the dried powder in Fig. 1 is different from that obtained from the oxalate coprecipitation by using metal carbonates as starting chemicals [22], where the precipitate was reported to consist of either individual metal oxalates or their solid solutions. During the calcination in air, the copper oxalate decomposed to CuO in the temperature range 230–260 °C. After completion of the reaction, only CuO peaks were observed, which indicates the CuO solid solution was formed in this temperature range. The CuO solid solution was dissociated to form the $BaCO_3$ phase at 400 °C and the Y_2O_3 phase at temperatures ranging from 500–600 °C. Accordingly, the powder calcined at 600 °C in air consists of an intimate mixture of Y_2O_3, $BaCO_3$, and CuO. The XRD pattern obtained after calcination at 600 °C in air coincides with that obtained from the oxalate coprecipitation of metal carbonates after calcining at 700 °C in oxygen [22].

Fig. 2 exhibits the effect of pH, which was varied by adding different amounts of dilute NH_3OH solution as the titrating agent, on the phase purity of YBCO sintered at 900 °C for 8 h in oxygen. Here, 160 ml

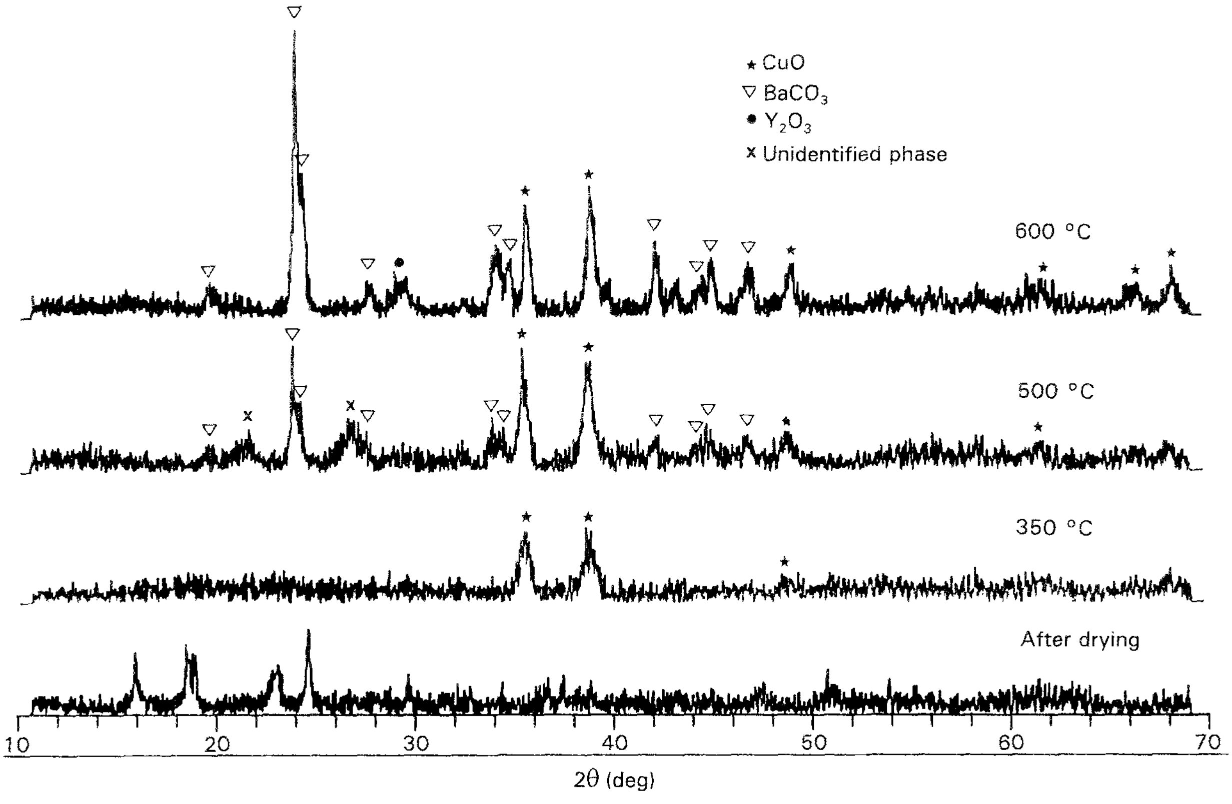

Figure 1 X-ray diffraction patterns of as-dried and calcined powders of YBCO, prepared by coprecipitation in oxalic acid, at different temperatures in air.

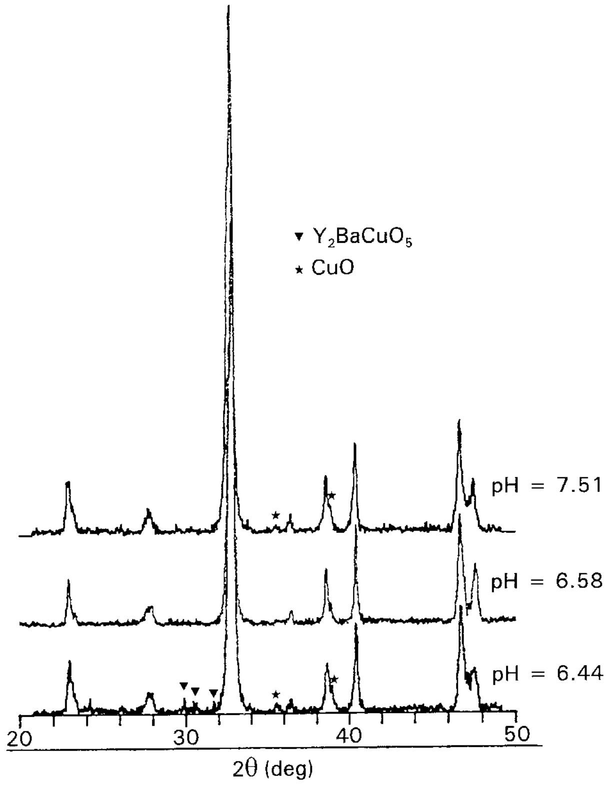

Figure 2 Influence of pH change, obtained by adding different amounts of dilute NH_3OH solution, on the phase purity of bulk YBCO after sintering for 8 h at 900 °C in oxygen.

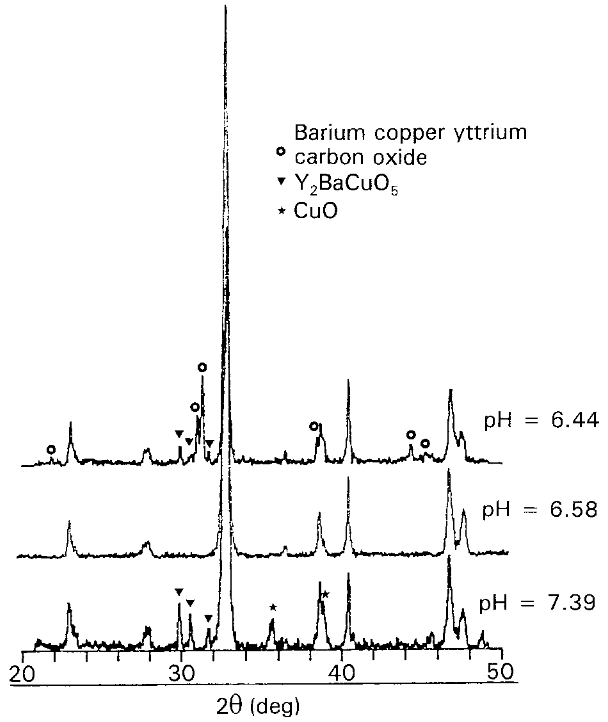

Figure 3 Influence of pH change, obtained by adding different amounts of 1 M anhydrous oxalic acid solution, on the phase purity of bulk YBCO after sintering for 8 h at 900 °C in oxygen.

anhydrous oxalic acid was used as a precipitant. As shown, the pH of 6.58, which was obtained by adding 60 ml dilute NH_3OH solution, led to the formation of a pure YBCO. As the pH was lowered to 6.44 with 55 ml dilute NH_3OH solution, Y_2BaCuO_5 (2 1 1) phase and the unreacted CuO were formed as impurity phases. As the pH was raised to 7.51 with 65 ml dilute NH_3OH solution, no 2 1 1 phase was found, but the unreacted CuO was found as an impurity.

The effect of pH change on the phase purity by adding different amounts of the titrating solution in Fig. 2 was not consistent with that by using different amounts of precipitant as shown in Fig. 3, where the pH was varied to 6.44, 6.58, and 7.39 by using 180, 160 and 135 ml 1 M anhydrous oxalic acid solution, respectively. In Fig. 3 the amount of the dilute NH_3OH solution was fixed at 60 ml throughout the coprecipitation processes. The amount of 1 M oxalic acid solution, required to convert the metal cations to oxalates, is 143 ml assuming that all the metal cations in the nitrate solution mixture were precipitated as oxalates. The use of 135 ml oxalic acid solution, which is less than the required amount, stemmed from the fact that the precipitates consisted of oxalates and nitrates in Fig. 1. Usually an excess amount of oxalic acid ranging from 13–80 vol % is added for the preparation of YBCO powder by the oxalate coprecipitation [16, 23, 24]. In Fig. 3 the pH of 6.44 caused barium copper yttrium carbon oxide ($Ba_{3.2}Cu_{1.7}Y_{0.8}O_{6.1} \cdot x\, CO_2$) and 2 1 1 phase to form as impurities and the pH of 7.39 resulted in the formation of the impurity phases of 2 1 1 and CuO.

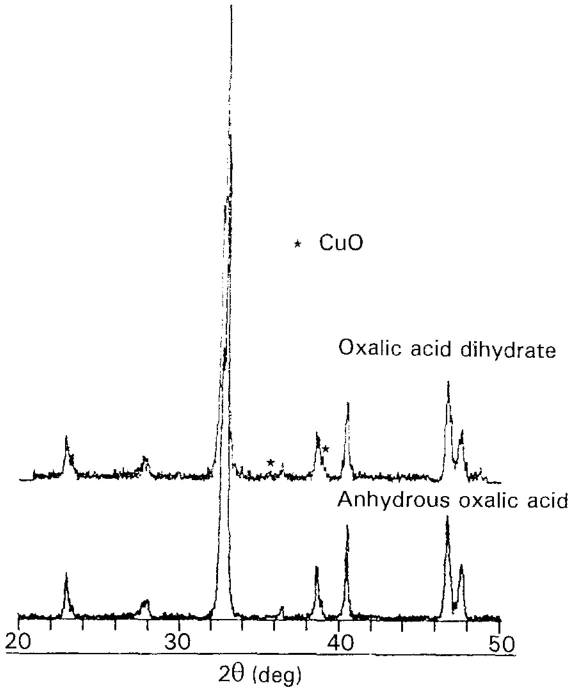

Figure 4 X-ray diffraction patterns of bulk YBCO, prepared by using different precipitants in coprecipitation processes, after sintering for 8 h at 900 °C in oxygen.

The phase purity of the YBCO also depended on the type of precipitant, Fig. 4. When the same amount (160 ml) of 1 M oxalic acid dihydrate solution was used as the precipitant instead of the anhydrous oxalic acid, there was only a slight change in the pH, that is, from 6.58 to 6.53, but the oxalic acid dihydrate produced the unreacted CuO. Even with the identical pH of 6.44 in Figs 2 and 3, which was obtained by adding different amounts of titrating agent and precipitant, the resultant phases were totally different. Thus the phase purity of YBCO did not directly depend on the pH of the coprecipitation process, but rather on procedures to change the pH.

The J_c of the samples in Figs 2 and 4 was plotted as a function of the magnetic field, Fig. 5. As expected, the minor impurity phases led to a drastic decrease in J_c of the bulk YBCO samples. At zero magnetic field the YBCO, prepared by precipitation in the oxalic acid dihydrate, exhibited the highest J_c. As the magnetic field was applied, however, YBCO, which was prepared using the anhydrous oxalic acid at pH 6.58, showed the highest value due to the absence of the impurity phases as expected from the XRD patterns in Figs 2–4. The sample of pH 6.44 gave the lowest J_c because of the existence of the 2 1 1 and CuO impurity phases. This indicates that the 2 1 1 phase is more detrimental to J_c than CuO. The XRD patterns of the samples of pH 7.51 in Fig. 2 and the samples obtained by using oxalic acid dihydrate in Fig. 4 show that there is a nearly same amount of CuO content in each sample. Nevertheless, the J_c values of these samples in the weak magnetic field were considerably different, Fig. 5. This implies that the amount of unreacted CuO content in YBCO is not a major factor in determining J_c, even though the existence of the impurity lowers J_c of bulk YBCO.

The YBCO samples, prepared with pH 6.58, were sintered at 900 °C for various times in oxygen and their J_c values are plotted in Fig. 6. The maximum J_c of 460 A cm^{-2} at zero field was obtained from the sample whose density was 4.96 g cm^{-3} by sintering for 5 h. At a magnetic field above 100 G, however, YBCO, (density 5.24 g cm^{-3}) on sintering for 8 h exhibited the highest J_c, followed by the sample with a density of 5.34 g cm^{-3} obtained by sintering for 10 h. This is consistent with the reports [5, 13] that J_c of YBCO is highest with an intermediate density, which optimizes the oxygenation of YBCO and the connectivity of the YBCO grains.

The sample with a density of 4.96 g cm^{-3}, whose diameter was 3.40 mm, was ground to a rectangle of 1.4 mm × 2.8 mm in order to determine the sample-dimension dependence of J_c. In accordance with the earlier reports [24, 25], J_c increased as the cross-sectional area of the specimen decreased, Fig. 6. The sample-dimension dependence of J_c disappeared in a magnetic field over about 100 G. Thus, J_c values in zero magnetic field do not represent the current transport property of bulk YBCO. This suggests that a comparison of the current transport property of the bulk YBCO samples should be made with J_c values measured in a magnetic field of 100 G or higher.

The 100 G values of J_c of the YBCO samples in Figs 2–6 are plotted as a function of orthorhombic distortion in Fig. 7. The orthorhombicity is governed by the oxygen content in YBCO and the phase purity of YBCO specimens [26]. A low oxygen content and the existence of non-superconducting phases results in a small orthorhombicity. The degree of orthorhombic distortion was determined by comparing the splittings of {2 0 0} and {1 2 3} peaks from the sintered samples with those from the YBCO powder of Wong-Ng *et al.* [27]. As shown in Fig. 7, there was a tendency for J_c determined in a magnetic field of 100 G to increase with increasing orthorhombic distortion. Accordingly, an optimal J_c of bulk YBCO can be obtained by increasing the orthorhombicity which depends on the properties of YBCO powders. Furthermore, the current transport property of bulk YBCO can be reasonably predicted by measuring the orthorhombic distortion of sintered samples from XRD data.

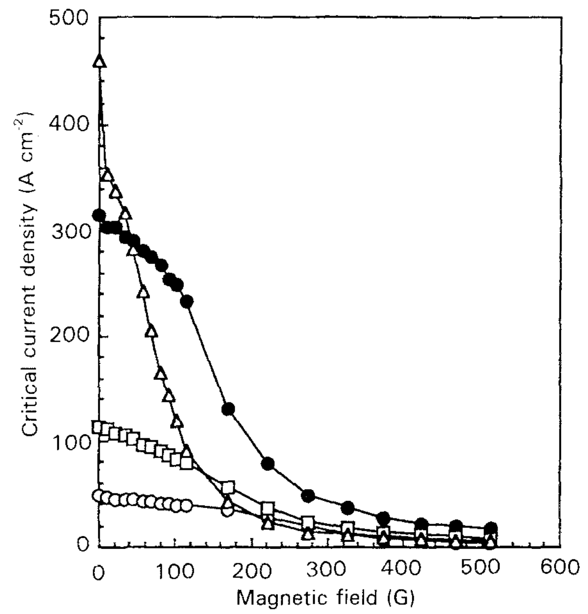

Figure 5 Critical current density at 77 K of the specimens in Figs 2 and 4 as a function of the magnetic field. pH: (○) 6.64, (●) 6.58, (□) 7.51 (△) Oxalic acid dihydrate.

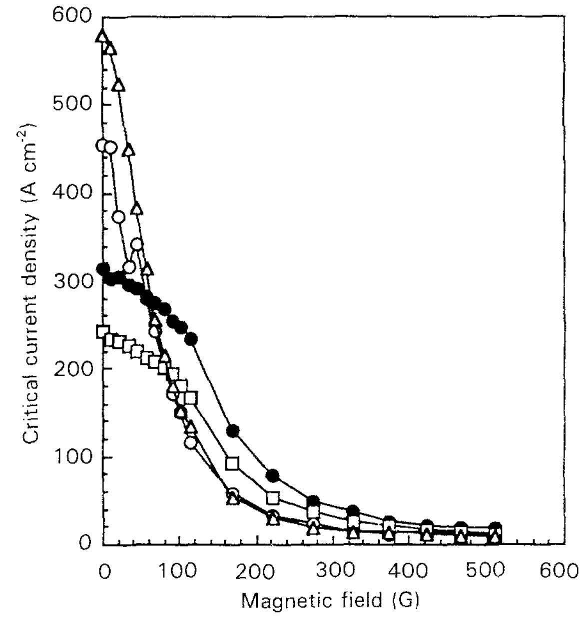

Figure 6 Influence of sample density of bulk YBCO on critical current density, J_c, at 77 K. The sample geometry dependence of J_c is shown for the specimen with a density of 4.96 g cm^{-3}. Density: (○) 4.96 g cm^{-3}, (●) 5.24 g cm^{-3}, (□) 5.34 g cm^{-3}: (△) 1.4 mm × 2.8 mm.

4. Conclusions

Optimal coprecipitation conditions for the preparation of YBCO single phase appeared to be the addition of excess amounts of barium (14 vol %) and

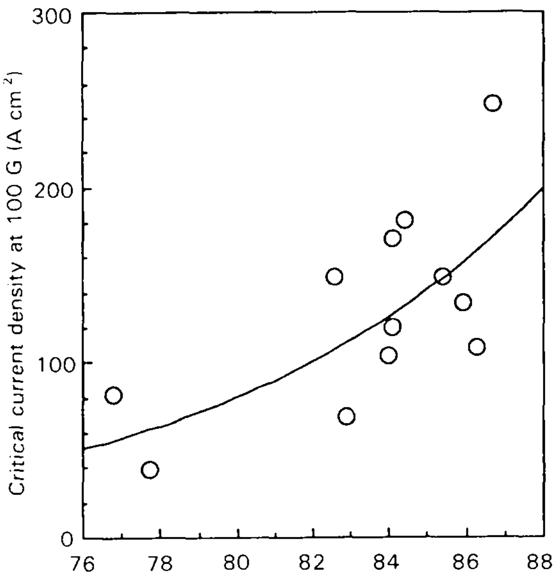

Figure 7 Critical current density at 77 K in a magnetic field of 100 G as a function of the degree of orthorhombic distortion of sintered bulk YBCO superconductors. A 100% distortion corresponds to a pure YBCO powder.

copper (12 vol %) nitrates and 12 vol % excess of the required anhydrous oxalic acid to convert the metal cations to oxalates and a pH of 6.6-6.7, which was obtained by adding 60 ml of a dilute ammonium hydroxide solution for a 663 ml nitrate solution mixture. It was shown that the J_c values of YBCO bulk samples measured in a magnetic field above 100 G eliminated the influence of the sample dimensions on the determination of J_c. The YBCO bulk specimen prepared from the optimally processed powder exhibited a critical current density, J_c, of 250 A cm^{-2} at 77 K in a low magnetic field of 100 G. It was observed that J_c of bulk YBCO superconductor in a magnetic field of 100 G tends to increase as the orthorhombic distortion increases. The orthorhombic distortion was high for the samples with pure YBCO phase and an intermediate density.

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