

On the simultaneous calcination and sintering of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in high magnetic fields

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Received 16 July 1993; in final form 4 October 1993; accepted 8 October 1993

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ was prepared from Y_2O_3 , BaCO_3 and CuO by calcination and sintering carried out in one step (without intermediate grinding and pressing) at 900°C and 12 T for 9 h. The resulting superconductor had higher J_c perpendicular to the magnetic field than parallel to the field. J_c perpendicular to the field was slightly larger than that for the case without a magnetic field and all J_c values were low due to the high porosity resulted from having no intermediate grinding and pressing. In contrast to previously published work, no crystallographic alignment was indicated by X-ray diffraction, so the degree of alignment of the c -axis texture parallel to the magnetic field was, if present, very small. We conclude that the method of calcination and sintering in a magnetic field for possible alignment of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystals is not practical.

1. Introduction

The discovery of the high- T_c superconducting ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ led to extensive studies over the past few years. However, the transport critical current density of these high-temperature bulk oxide superconductors is at present still rather low. The superconductive phase is orthorhombic in crystal structure, such that the $[\text{CuO}_2]$ a - b plane with copper in the distorted square planar coordinate leads to superconductivity [1-4].

On the basis of the anisotropic electrical conductivity of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystal, several approaches have been taken to orient the grains for the purpose of enhancing the critical current density (J_c). These approaches include metallurgical methods, such as melt texturing and directional solidification [5,6], mechanical methods, such as pressing, forging, and rolling [7], as well as physical methods, such as magnetic grain alignment [8]. In the case of magnetic grain alignment, the intrinsically anisotropic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ powders were subjected to a magnetic field for the sake of grain alignment and then pressed and sintered into a dense pellet [9]. In this paper, another related method, namely simultaneous calcination and sintering in high magnetic fields, was used to align the crystals. Like the magnetic grain

alignment method, the method of simultaneous calcination and sintering uses a magnetic field to effect grain alignment. However, the main difference is that, instead of magnetic alignment of the already calcined $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ powders, the precursor materials (namely a mixture of Y_2O_3 , BaCO_3 , and CuO powders) were both calcined and sintered under a magnetic field. During magnetic calcination, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ grains were formed under a magnetic field.

Without experimental data, Rybka [10] claimed in a 1990 patent that by applying a magnetic field (1-10 T) during bulk superconductor synthesis, "the high degree of grain orientation could be induced" and "the current density can be equivalent to or exceeding many of the existing superconducting materials". However, to date no publication other than this patent had been found that reported how T_c , J_c and other properties were changed after calcination in a magnetic field. To further explore the potential possibility of this method, we extended Rybka's work by calcining and sintering the samples at an even higher magnetic field (12 T) and subsequently characterizing the samples in terms of the crystallographic preferred orientation and J_c parallel and perpendicular to the applied magnetic field. Comparison

was made between samples calcined in the presence and absence of a magnetic field.

2. Experimental procedure

The Y_2O_3 (99.99%), $BaCO_3$ (99.99%) and CuO (99.999%) powders (all from Johnson Matthey Chem. Ltd., UK) were used to synthesize polycrystalline $YBa_2Cu_3O_{7-x}$. The processing procedure in this work is different from the traditional method. The traditional method for preparing bulk $YBa_2Cu_3O_{7-x}$ superconductor involves (i) calcining the mixed Y_2O_3 , $BaCO_3$ and CuO powders, (ii) grinding the reacted powder, (iii) compressing the reacted powder into a dense pellet, and (iv) sintering the pellet in flowing oxygen. However, since the purpose of this work is to let the superconductor crystallize in a magnetic field, the calcination and sintering were carried out in one step, i.e. without grinding between calcination and sintering.

The normal operating condition of the Bitter magnet used was that the temperature of the inner wall of the magnetic channel must be less than $40^\circ C$. Thus, a special tube furnace was made, as shown in fig. 1. In addition to having a thermally insulating material around the heating element in the furnace, a water-cooled metal coil was wrapped around the furnace to shield the heat radiation of the furnace.

The process of calcination and sintering in a mag-

netic field was conducted in the National Magnetic Laboratory in Cambridge, MA. Appropriate amounts of Y_2O_3 , $BaCO_3$ and CuO were mixed and then compressed under a pressure of 350 MPa into pellets of diameter 25.4 mm and thickness 1 mm. The pellets were then put on an Al_2O_3 plate, which was horizontally placed into the center of the tube furnace, which had been placed in the center of the magnetic channel. The samples were heated in flowing O_2 at $940^\circ C$ for 9 h. Due to the vast amount of electric power ($> 9 \times 10^3$ kV A) required to obtain the magnetic field and maintain regulation of the magnetic equipment, the calcination and sintering time was limited to 9 h. In order to avoid sample deformation due to the temperature non-uniformity, the heating rate was controlled at $8-10^\circ C/min$ and the cooling rate was controlled at $4-5^\circ C/min$. During calcination and sintering, when the temperature was above $800^\circ C$, a magnetic field of 12 T was applied. Comparison samples were prepared by using the same method except that no magnetic field was applied. The samples were also prepared using the traditional method. The procedure of the traditional method was: (i) calcining the mixed Y_2O_3 , $BaCO_3$, and CuO powders in air at $935^\circ C$ for 18 h, (ii) grinding the reacted powder, (iii) compressing the reacted powder into a pellet, and (iv) sintering the pellet in flowing oxygen at $950^\circ C$ for 24 h. The heating and cooling rates were controlled at $5^\circ C/min$ in the traditional method.

In order to measure the critical temperature (T_c) and critical current density (J_c), the samples were cut into $12\text{ mm} \times 4\text{ mm}$ pieces, with the longest edge of each piece either parallel or perpendicular to the direction of the magnetic field. The four-probe technique was used to measure T_c . The electrical contacts on all samples were made using silver paint, which was subsequently air dried. In measuring J_c , the current was smoothly introduced into the sample until a potential difference arose, indicating that a non-zero resistance had appeared. J_c was measured at 77 K.

X-ray diffraction (XRD) was used to identify the phase and possible crystallographic preferred orientation. Scanning electron microscopy (SEM) was used to examine the microstructure.

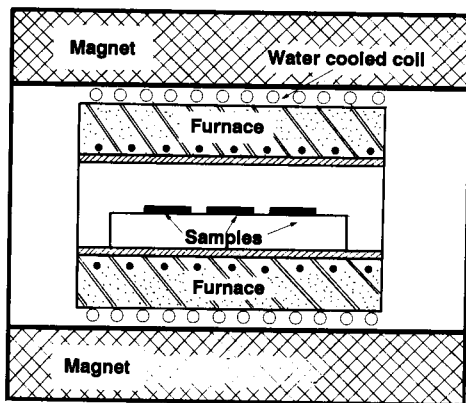


Fig. 1. Schematic representation of the experimental setup for magnetic calcination and sintering of the $YBa_2Cu_3O_{7-x}$ superconductor.

3. Results and discussion

The XRD patterns of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ obtained by calcination and sintering with and without a magnetic field are shown in figs. 2a and 2b, respectively. Fig. 2c shows the XRD pattern of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ prepared by the traditional method, which involved a much longer time of calcination and sintering. The patterns in figs. 2a and 2b are essentially identical, indicating that the magnetic field essentially did not cause crystallographic alignment. The XRD peaks are stronger (with a better signal-to-noise ratio) in fig. 2c than in fig. 2a or 2b. This is because of the

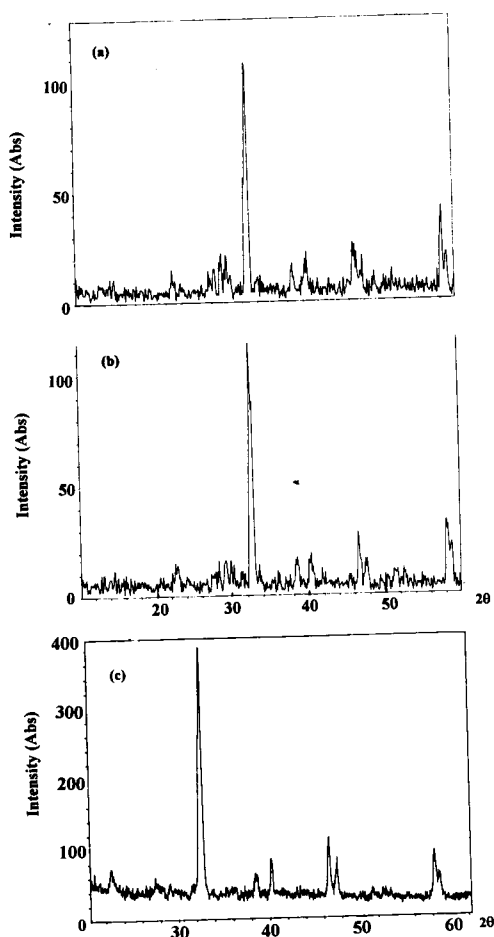


Fig. 2. X-ray diffraction patterns of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ bulk materials. (a) Synthesized in a magnetic field. (b) Synthesized with no magnetic field. (c) Synthesized by the traditional method.

much longer time of calcination and sintering in the traditional method.

Table 1 shows the measured results of T_c and J_c parallel and perpendicular to the direction of the magnetic field and for the case without a magnetic field during calcination and sintering. Each datum was the average value of two samples.

From table 1, we can see that the critical temperature T_c was essentially the same for the three cases whereas J_c parallel to the magnetic field (4.7 A/cm^2) was smaller than that perpendicular to the magnetic field (9.4 A/cm^2), which was slightly larger than that for the case without a magnetic field (8.3 A/cm^2). The a - b plane is the superconducting plane. The J_c results suggest that the magnetic calcination and sintering caused the c axis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ to be preferentially parallel to the magnetic field, even though no crystallographic alignment was observed by XRD. The sensitivity for crystallographic alignment may be lower for XRD than for J_c measurements. The direction of alignment is consistent with that of the magnetic grain alignment method, for which that the grains are aligned with the c axis oriented in the magnetic field direction [9].

The absolute values of J_c in table 1 are quite small. This is mainly due to the high porosity of the samples. Figs. 3a and 3b are the SEM photographs of the microstructure of the samples synthesized with and without a magnetic field, respectively. There is almost no microstructural difference between the two photographs. Very high porosity can be seen from fig. 3. Since no grinding was carried out between calcination and sintering in order to maintain the crystallographic orientation, it was difficult to densify the material. Thus, this method's main drawback is that the high porosity overshadows the effect of the grain alignment and therefore limits the potential of attaining high J_c .

Table 1
Results of critical temperature (T_c) and critical current density (J_c)^{a)}

Samples synthesized	T_c (K)	J_c (A/cm^2)
magnetic field	81.5 ± 2	4.7 ± 0.8
⊥ magnetic field	83.3 ± 1	9.4 ± 0.3
no magnetic field	82.7 ± 1	8.3 ± 0.3

^{a)} Average data of two samples.

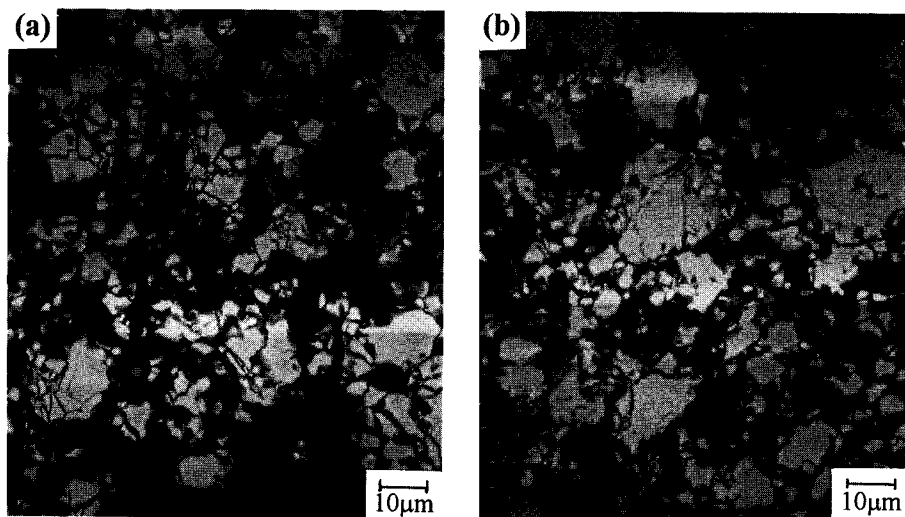


Fig. 3. SEM photographs of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ bulk materials. (a) Synthesized in magnetic field. (b) Synthesized with no magnetic field.

The nucleation and growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystals require the temperature to be above about 900°C . Therefore, the magnetic field must be applied during the high temperature synthesis in order to align the crystals as they grow. However, the higher the temperature, the greater the thermal vibration of the nuclei and the less the atoms' response to the magnetic field (in spite of the high magnetic field). Therefore, the tendency for grain alignment is very limited.

4. Conclusion

The effect of simultaneous calcination and sintering of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor in high magnetic fields was studied. The J_c parallel to the magnetic field was smaller than that perpendicular to the magnetic field, which was slightly larger than that for the case without a magnetic field. This indicates that the grains aligned to some extent with the c axis parallel to the magnetic field during calcination and sintering. However, the absolute values of J_c were very low, due to the high porosity, resulting from the absence of intermediate grinding steps between calcination and sintering. Since, at the high temperature, the nuclear thermal vibration largely disturbed the effect of magnetic field, the usefulness of calcination and sintering in a magnetic field

was limited. XRD and microstructural examination failed to provide evidence for crystallographic alignment (texture). Moreover, the cost of producing and maintaining the high magnetic field for a long period (9 h in this work) is high. We conclude that the method of calcination and sintering in a magnetic field for possible alignment of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystals is not practical.

Acknowledgement

This work was supported by the New York State Institute for Superconductivity, in conjunction with the New York State Energy Research and Development Authority. The technical assistance of Mr. Zhenqiang Shi of the State University of New York at Buffalo is appreciated.

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