Physical and electromagnetic properties of Y-Ba-Cu-O superconductors synthesized with peroxides

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The physical and electromagnetic properties of Y-Ba-Cu-O superconductors synthesized with BaO_2 (barium peroxide) have been studied. A comparison of reactions with $BaCO_3$ and BaO indicates that the peroxide promotes formation and strong alignment of platelet grains in planes normal to the c axis, yields material with larger grain sizes and aspect ratios, reduces the synthesis reaction time by over half, increases the volume fraction of material that goes superconducting (Meissner effect), and facilitates metallic conduction in the normal state. Critical current densities of 1.1×10^4 A/cm^2 at 77 K have been observed in peroxide-synthesized material. These beneficial effects may be due to the low melting temperature of BaO_2 (450 °C), and the elimination of residual unreacted $BaCO_3$, BaO, and/or C.

I. INTRODUCTION

Because of its simplicity, the solid-state reaction for bulk materials remains a basic method of synthesis for high-temperature superconductors despite the large number of alternate methods reported in the literature.[1] Similarly, because of their stability and availability in pure form, carbonates of barium, strontium, and calcium continue to be used in the three major systems (Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, and Tl-Ba-Ca-Cu-O). However, calcination must be used to drive off the unwanted carbon, and residual amounts of carbon and/or unreacted carbonate remain behind especially at grain boundaries, resulting in deleterious effects on such parameters as critical current density (J_c).[2] Thus, carbon-free starting materials such as peroxides are increasingly of interest in the synthesis process.

Although peroxides tend to be unstable, and commercially available materials impure, several investigators have reported the preparation of Y-Ba-Cu-O using BaO_2 instead of $BaCO_3$. See for example the references in Hepp *et al.*[3] Indeed, Hepp *et al.* report that the use of BaO_2 routinely produces more homogeneous, metallic, and dense material, along with increased reaction rates. Our own investigations, reported here, generally confirm such observations.

Experiments undertaken with BaO_2 to prepare $Y_1Ba_2Cu_3O_{7-x}$ indicate the propensity of BaO_2 to promote the formation and strong alignment of platelet crystallites in planes normal to the c axis which can lead to increased J_c, to reduce the synthesis time by over half, and to facilitate metallic conductivity in the normal state. Additionally, we have found that BaO_2 promotes grain size growth and increases the volume fraction of material that goes superconducting (Meissner effect). However, we have not seen an increase in the density of the material with the use of BaO_2, although that property may be a function of reaction temperature, a variable we did not investigate.

II. EXPERIMENT

Six reactions were studied as shown in Table I. We felt it necessary to include a BaO control reaction to test the effica-

cy of BaO_2. In addition, in order to vary the amount of oxygen present in the starting reactants, we included cuprous oxide, Cu_2O. The "best" results were found with BaO_2 and CuO, and the "worst" results with BaO and Cu_2O.

Y_2O_3 (99.99%), $BaCO_3$ (99.9%), BaO (93%), BaO_2 (88%), CuO (99.999%), Cu_2O (99.9%) were obtained from standard commercial suppliers. The balance of the BaO and BaO_2 composition was carbonate and was taken into account as such in the ratio formulation of the elements for the synthesis. The powders were ground with an alumina mortar and pestle, and fired in alumina crucibles.

The reaction conditions were kept constant throughout and consisted of an initial calcination in air at 925 °C for 12 h, a grinding to a powder, a subsequent reaction in air at 925 °C for 12 h with a further grinding to a powder, pellet formation at 40–60 kpsi with a sintering in air for 1 h at 925 °C, and a final anneal in air for 5 h at 550 °C with a furnace cool to room temperature. Pellet size was typically 12 mm in diameter and 1 mm thick. 925 °C was chosen as the reaction temperature based on a report that this was an optimum processing temperature, yielding the least number of unwanted phases.[4] It was kept constant throughout the study in order to minimize the influence of this variable.

X-ray diffraction established that the materials synthesized with $BaCO_3$, BaO_2, or BaO had orthorhombic crystal structure.[5]

TABLE I. Reactions studied experimentally.

$Y_2O_3 + 4BaCO_3 + 6CuO \rightarrow 2(YBa_2Cu_3O_{6.5}) + 4CO_2$
$Y_2O_3 + 4BaCO_3 + 3Cu_2O \rightarrow 2(YBa_2Cu_3O_5) + 4CO_2$
$Y_2O_3 + 4BaO_2 + 6CuO \rightarrow 2(YBa_2Cu_3O_{8.5})$
$Y_2O_3 + 4BaO_2 + 3Cu_2O \rightarrow 2(YBa_2CU_3O_7)$
$Y_2O_3 + 4BaO + 6CuO \rightarrow 2(YBa_2Cu_3O_{6.5})$
$Y_2O_3 + 4BaO + 3Cu_2O \rightarrow 2(YBa_2Cu_3O_5)$

Superconducting phase
$YBa_2Cu_3O_{7-x}$
$0 < x < 0.6$
Orthorhombic perovskite

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III. RESULTS AND DISCUSSION

A. Physical properties

A strong processing-related alignment of the grains was observed through x-ray diffraction, using a Rigaku computer-controlled diffractometer. Figure 1 shows the strong set of (002), (003), (005), and (006) peaks, indicative of align-
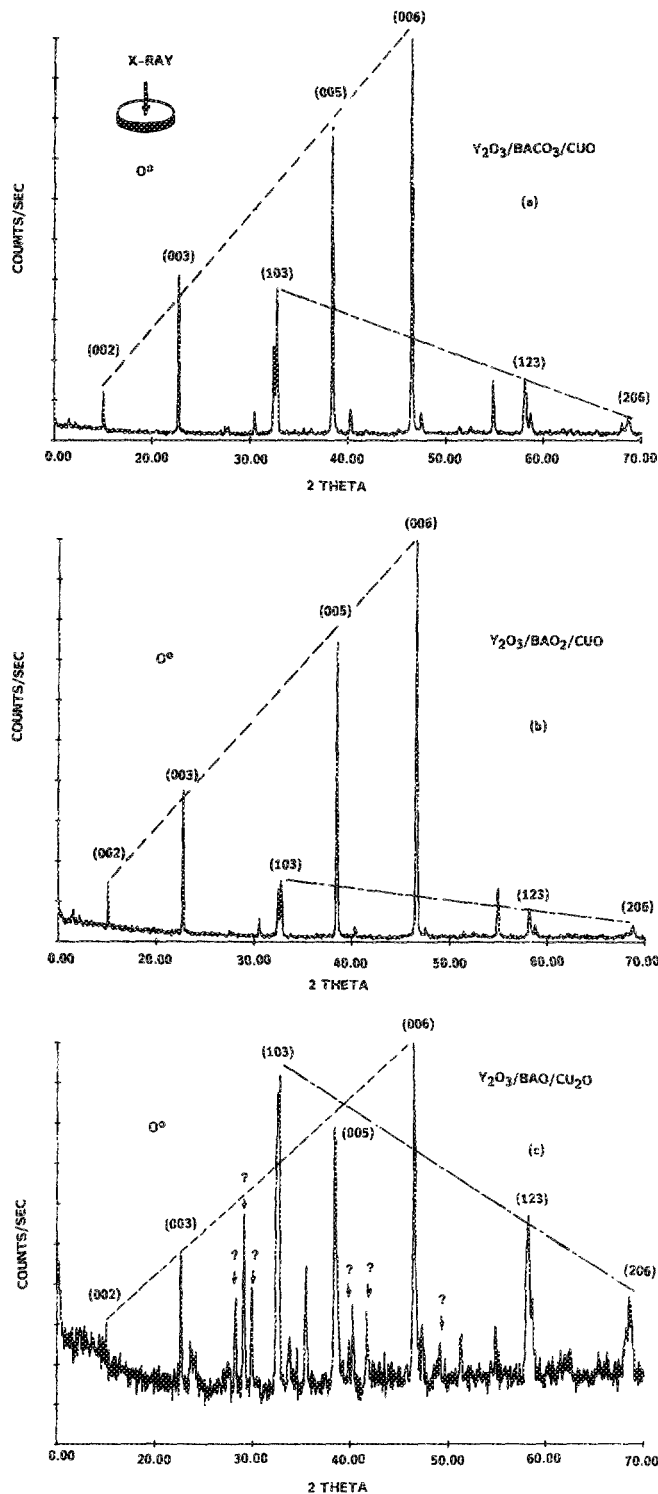

FIG. 1. X-ray diffraction patterns for the (a) $BaCO_3$/CuO, (b) BaO_2/CuO, and (c) BaO/Cu_2O reactions, with the beam incident normal to the pellet face.

ment normal to the c axis, relative to the normally strong (103), (123), and (206) peaks in randomly oriented isotropic material. The x-ray beam was incident on the top face of the pellet—the face normal to the uniaxial compression direction. X-ray diffraction taken parallel to the pellet face (designated as 90°) was marked by an almost complete absence of the (00l) peaks. Thus the alignment is not a surface effect.[6] The strongest alignment was observed with the BaO_2/CuO reaction [Fig. 1(b)], and the poorest occurred with BaO/Cu_2O, where a large number of unwanted phases appeared [Fig. 1(c)]. Our experience with BaO was the opposite of that reported by Wu and Ruckenstein.[7]

Scanning electron micrographs of the pellet faces (0°) and surfaces normal to these faces (90°), using a JEOL scanning electron microscope, revealed the presence of platelet-shaped crystallites and their alignment. Typical micrographs for the BaO_2/CuO and BaO/CuO reactions are shown in Figs. 2(a) and 2(b), respectively. Grain sizes were largest with the BaO_2/CuO reaction, approximately in the 10–30-μm range, dropping to 2–5 μm with the BaO reactions. A summary of the results obtained for the various reactions is provided in Table II.

In the case of the BaO_2 reactions, the reacted mass after the first firing or calcination was found to be sufficiently dense and cohesive that it was tested for superconductivity. Magnetic susceptibility measurements indicated a T_c of approximately 90 K, but poorly formed material. Scanning electron micrographs revealed an open porous structure consistent with the susceptibility measurements. However, the second reaction at 925 °C could be eliminated, and the final pellet sintered without any detrimental effect on its quality. Thus the use of peroxides allowed the reaction time to be reduced by approximately half. These observations are consistent with the fact that BaO_2 has a lower decomposition temperature and melts at about 450 °C and thus should facilitate more vigorous reaction of the powders. In addition, the stoichiometry of the BaO_2/CuO reaction in Table I indicates the highest mole ratio of oxygen at 8.5, which could minimize the need for external oxygen depending on the nature of the reaction vessel.

A single carbon content analysis using a Perkin-Elmer CHN analyzer indicated that carbon was still present with the peroxide-reacted materials, but at the level of about half (by weight %) of that in the carbonate-reacted materials. The results obtained are listed in Table II. This is consistent with the fact that the starting BaO_2 was only 88% pure, the balance being largely carbonate. In addition, the BaO-reacted materials appeared to contain almost as much carbon as the carbonate-reacted materials, although the starting BaO was purportedly 93% pure.

Densities of the sintered pellets ranged from 4.3 to 4.9 g/cm^3 with no indication that the peroxides promoted densification. The theoretical density is 6.38 g/cm^3.[8] This is contrary to the results of Hepp et al.,[3] who reported achieving 85% of theoretical density with BaO_2 but only 60% with $BaCO_3$. The reason for this difference is unknown, although processing temperature and pressing pressure are probably a factor.[9] As noted earlier, we elected to keep the processing temperature fixed at 925 °C based upon a report that this was

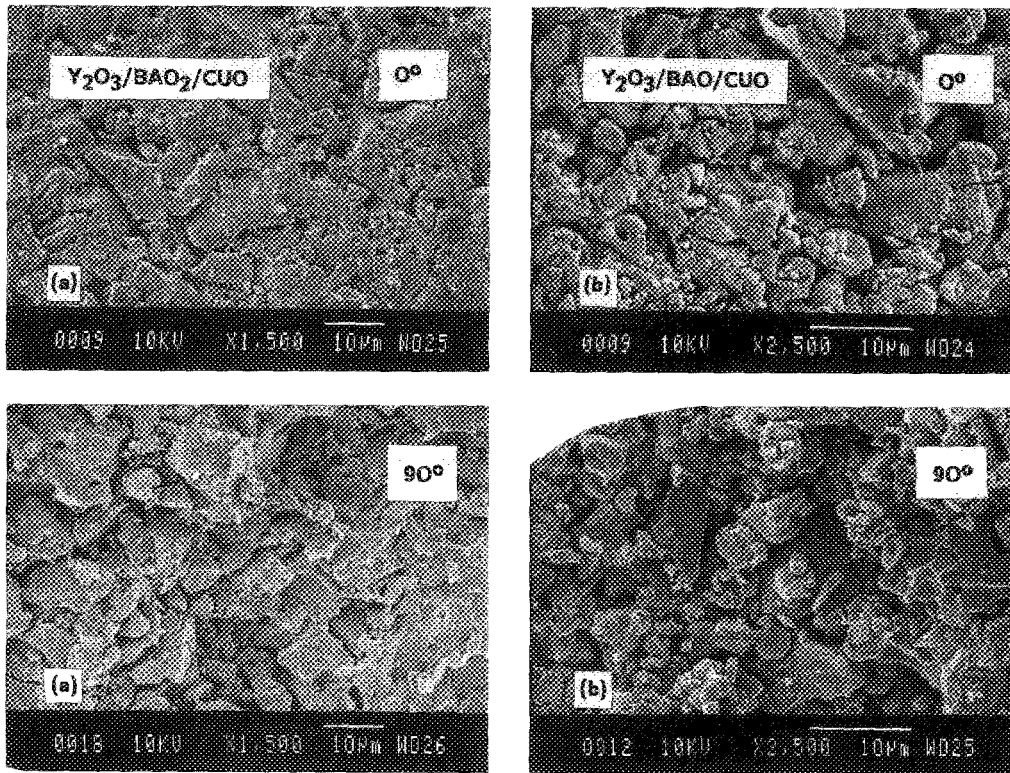7489   J. Appl. Phys., Vol. 67, No. 12, 15 June 1990

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FIG. 2. Scanning electron micrographs of pellet faces (0°) and surfaces normal to these faces (90°) for the (a) BaO_2/CuO reaction at $\times 1500$ magnification and (b) BaO/CuO reaction at $\times 2500$ magnification.

an optimum temperature yielding the least number of unwanted phases.[4]

B. Electromagnetic properties

Magnetic susceptibility measurements as a function of temperature indicated that the greatest volume fraction of material to go superconducting occurred with the BaO_2/CuO reaction and the least with the BaO/Cu_2O reaction. Typical data for the CuO set of reactions, taken on a Quantum Design magnetometer, are shown in Fig. 3. Measurements were made with a field of 150 G. The saturation value

of the moment at low temperatures is taken as a qualitative indicator of the volume fraction that undergoes superconductivity. The T_c onsets for the BaO_2 and the $BaCO_3$ reactions were typically in the 90–93-K range, and there was no indication that BaO_2 promoted an increase in T_c. However, the T_c onsets for the BaO reactions were markedly reduced, being as low as 80 K for the BaO/Cu_2O reaction. In addition, all the BaO reactions showed a softer increase in diamagnetism with decreasing temperature after T_c onset. The experimental data are summarized in Table III.

Resistivity measurements as a function of temperature, using the conventional four-contact method with a measure-

TABLE II. Summary of measured physical properties for the reactions in Table I.

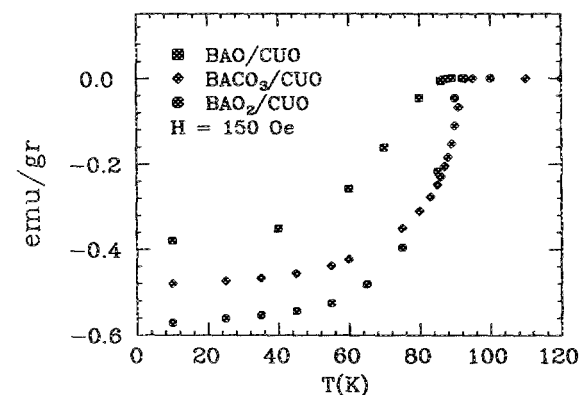|	Density[a] (gm/cm^3)	Grain orientation (x ray)	Grain size (μm)	Carbon content (wt. %)
$BaCo_3/CuO$	4.55	yes (strong)	5–10	0.10
$BaCO_3/Cu_2O$	4.65	yes (weak)	5–10	0.12
BaO_2/CuO	4.65	yes (very strong)	10–30	0.06
BaO_2/Cu_2O	4.53	yes (strong)	5–20	0.07
BaO/CuO	4.28	? (very weak)	2–5	0.09
BaO/Cu_2O	4.94	yes (weak) (other phase)	2–5	0.10

[a] Theoretical density: 6.38 g/cm^3.

FIG. 3. Magnetic moment (susceptibility) as a function of temperature for the three reactions indicated.

TABLE III. Summary of measured electromagnetic properties for the reactions in Table I.

	T_{c_0} [a] (K)	X [b] (emu/g)	T_{ρ_0} (K)	ρ (above T_c)
BaCO$_3$/CuO	93	0.48	91	semiconducting
BaCO$_3$/Cu$_2$O	91	0.45	82 (tail)	semiconducting
BaO$_2$/CuO	91	0.57	89	metallic
BaO$_2$/Cu$_2$O	90	0.54	85	metallic
BaO/CuO	87	0.38	83	semiconducting
BaO/Cu$_2$O	80	0.35	<77	semiconducting

[a] From susceptibility measurements.
[b] Saturation value at low T.

ment system having a resolution of 10^{-6} Ω cm, showed sharp transition to zero resistance ($\Delta T = 2$–4 K) with the CuO reactions, but long tails with the Cu$_2$O reactions. For example, zero resistance did not occur until 82 K (T_{ρ_0}) with the BaCO$_3$/Cu$_2$O reaction. A typical profile for the BaO$_2$/CuO reaction is given in Fig. 4(a). The BaO$_2$ reactions were notable for their display of metallic conduction in the normal state (increasing slope with increasing temperature). The carbonates yielded semiconducting behavior, however [see Fig. 4(b)]. This is consistent with the fact that there should be less BaCO$_3$ and C residuals in reactions using BaO$_2$. Experimental resistivity data are also summarized in Table III.

It is interesting to speculate on the driving force which causes the strong grain alignment with the BaO$_2$/CuO reac-
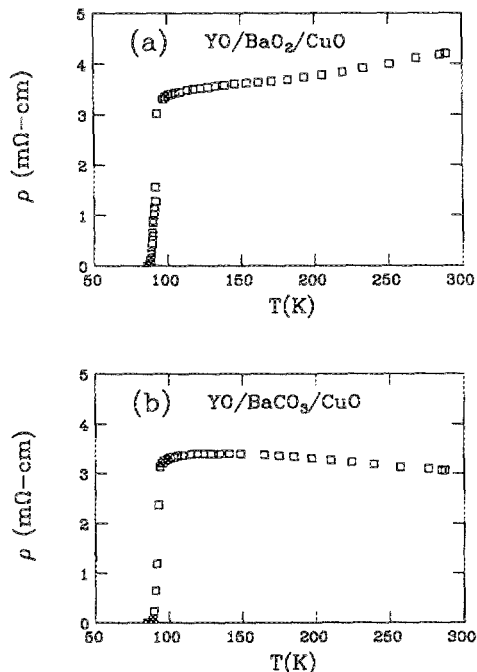

FIG. 4. Resistivity as a function of temperature for the (a) BaO$_2$/CuO and (b) BaCO$_3$/CuO reactions.

tion. The powder produced after either the calcination or the second reaction, but prior to pelletization (sintering), contains grains with an aspect ratio of about 3:1 (platelets). This aspect ratio was largest with the BaO$_2$/CuO reaction and smallest with BaO/Cu$_2$O reaction where the grains were more spherical in nature. Nearly isotropic grains are expected when growth is controlled by mass-transport diffusion rather than growth kinetics, even though the c-axis growth rate is slow compared to the a and b axes in the Y-Ba-Cu-O system.[10] In the case of BaCO$_3$ a liquid eutectic forms at approximately 930 °C,[9] with platelets resulting from the enhanced a-b plane growth rate. Due to a low melting temperature of approximately 450 °C, BaO$_2$ can act like a flux, enhancing both grain aspect ratio and size. On the other hand, BaO with a high melting temperature of about 1920 °C, creates a diffusion-limited environment with small spherical grains forming. During compression and subsequent sintering to form the pellet, the platelets are oriented with the a-b planes perpendicular to the stress applied along what is to become the pellet c axis. The alignment process may be facilitated by the low 450 °C melting temperature of residual BaO$_2$.

Grain alignment is known to promote a large increase in J_c, especially with thin-film depositions[11] where values of 10^6 A/cm^2 have been observed compared to 10^3 A/cm^2 for bulk unaligned material. High-J_c values are essential for practical applications such as wires. Preliminary measurements of J_c on barlike structures approximately 0.5×0.5 mm in cross section from the BaO$_2$/CuO reaction have yielded values of 1.1×10^4 A/cm^2 at 77 K. This is comparable to that reported by Jin et al.[2] on melt-grown material where the improvement was attributed, in part, to preferentially aligned microstructure. J_c values were only about 10^3 A/cm^2 with material from the BaCO$_3$/CuO reaction. More recently, J_c values as high as 7.5×10^4 A/cm^2 have been observed for liquid-phase processed material in which the improvement was again attributed to grain orientation.[12] Our results on J_c will appear separately.[13]

Consistent with the improvement in the physical properties of the resulting compounds, BaO$_2$ also improves electromagnetic properties. Besides yielding the highest volume fraction of material to go superconducting, the peroxide promotes metallic conduction in the normal state. Both of these improvements can be ascribed in part to the reduction of residual BaCO$_3$ and C at grain boundaries. Similarly, the poor results with BaO are likely the effect of residual unreacted BaO which has a high melting temperature of 1920 °C. In addition, the BaO$_2$/CuO reaction has the highest mole ratio of oxygen, as noted earlier. Oxygen stoichiometry is known to control the temperature variation of resistivity in the normal state, with metallic conduction occurring with the highest oxygen concentrations.[14]

We have kept the synthesis conditions the same for all six reactions so that a direct comparison could be made of the properties of the end product. It could be argued that the carbonate material was only "half-cooked" in comparison to the peroxide material, and that more heat/grind cycles would make the carbonate material

comparable to the peroxide material. We have found this not to be the case. The properties reported in this paper changed little upon several such additional heat/grind cycles.

IV. CONCLUSION

In general, there appears to be ample evidence for the beneficial effect of peroxides in the synthesis of high-temperature superconductors. Certainly, synthesis times can be greatly reduced by eliminating the "calcination" stage needed with carbonates, and there is a considerable improvement in J_c. There appears to be no merit to the use of BaO or Cu_2O. However, further careful and detailed work is required to quantify these results, especially with reaction temperature as a variable.

ACKNOWLEDGMENTS

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