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SYNTHESIS OF CERAMIC SUPERCONDUCTORS UNDER LOW OXYGEN PRESSURE

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Abstract

We have developed a process for synthesizing orthorhombic $YBa_2Cu_3O_x$ ("123") superconducting powders, which involves calcination of the precursor powder under reduced total oxygen pressure. Because a single calcination at 800°C for 4 h in flowing oxygen with a pressure of 2 mm Hg results in essentially phase-pure material, total calcination times have been drastically reduced. At liquid nitrogen temperature, sintered pellets made from this powder have critical current densities of ~1000 A/cm^2 in zero applied magnetic field.

Keywords: synthesis, improved calcination, low-pressure

1. Introduction

High-temperature ceramic superconductors are normally prepared via a solid state reaction from a mixture of precursors, such as oxides, carbonates, and/or nitrates. The mixed precursors are calcined at 900-950°C for 50-100 h with intermittent grindings [Goretta, et al., 1988]. The high calcination temperatures used in this conventional method result in the formation of liquid phases and some nonsuperconducting phases such as Y_2BaCuO_5 and $BaCuO_2$. During calcination, the CO_2 released by decomposition of $BaCO_3$ can, however, react with 123 to form $BaCO_3$, Y_2O_3, CuO and $Y_2Cu_2O_5$, depending on temperature [Fjellvag, et al., 1988]. The presence of these nonsuperconducting phases, especially at grain boundaries, lowers critical current density (J_c) [Shi, et al., 1988]. In addition to producing these undesirable phases, the process is very time-consuming and results in coarse particles. Partial vacuums have been utilized by other investigators to calcine powders and to sinter polycrystalline bodies [Uno, et al., 1988, and Lay, 1989]; however, in all cases multiphase materials were obtained. We report here a synthesis route to obtain essentially phase-pure orthorhombic 123 powders at 800°C in flowing O_2 at reduced pressure.

2. Experimental methods

Required amounts of Y_2O_3, $BaCO_3$, and CuO were wet-milled for about 15 h in methanol. The resultant slurry was pan-dried in air, ground in an agate mortar, and heated at a rate of ~20°C/h in the temperature range of 700-800°C in flowing O_2 with a pressure of 2 mm Hg and held for 4 h at 800°C. During cooling, the vacuum was discontinued and ambient-pressure O_2 was passed. A 3-h hold at 450°C was incorporated into the cooling schedule to promote oxygenation of the resulting powder. A Fourier transform infrared (FTIR) spectrometer was used to monitor the evolution of CO_2 during calcination. Heating and O_2 flow rates were adjusted to maintain various levels of CO_2 during calcination. The calcined powders were characterized by thermal analyses and X-ray diffraction.

3. Results and discussion

Thermogravimetric analysis (TGA) showed the beginning of the weight loss attributable to CO_2 evolution during heating the precursor powders at the ambient pressure of one atmosphere at about 750°C; however, at 2 mm Hg, it begins at about 620°C. Under reduced total pressure, decomposition is essentially completed at ~800°C, where as under ambient pressure, decomposition is not complete even at ~1000°C. Heating powders at ~20°C h^{-1} in the range of 700-800°C enabled CO_2 levels, as measured by FTIR, to be maintained at less than 2% of the oxygen level. At 900°C under ambient pressure, the calculated thermodynamic equilibrium partial pressure of CO_2 at which 123 becomes unstable is ~2% CO_2 in the oxygen atmosphere [Fjellvag, et al., 1988]. Faster heating rates resulted in higher CO_2 concentrations and yielded powders containing Y_2BaCuO_5 and other impurity phases. Endothermic or exothermic reactions or melting events associated with impurity phases were identified by differential thermal analysis DTA [Goretta, et al., 1988]. As shown in Fig. 1, for the powder calcined once at 800°C in low pressure, the only event observed was a change in slope caused by conversion of the powder from orthorhombic to tetragonal upon heating (curve a). Conventionally processed powder (calcined three times at 900°C under ambient pressure) exhibited an endotherm at ~940°C caused by melting of a CuO-$BaCuO_2$ eutectic (curve b).

These DTA traces were obtained in flowing oxygen at ambient pressure.

The 123 powder processed at low pressure was also shown to be phase pure by X-ray diffraction (Fig. 2). Analysis of the orthorhombic-peak split and comparison against published data [Wong-Ng, et al., 1987] revealed no tetragonal phase in the powder. Particle size resulting from the low-pressure synthesis was 1 to 4 µm. This relatively small particle size is due to the low processing temperature. Calcination could be carried out at 800°C, rather than 900°C or higher, because cation diffusional kinetics in 123 are faster under reduced O_2 pressures [von Stumberg, et al., 1989]. A partial vacuum was used instead of a mixture of O_2 and a noble gas, because CO_2 was removed with increased efficiency.

The resultant 123 powder was cold-pressed into pellets that were capable of levitating magnets. These pellets were then sintered in O_2 to make dense superconductors. For sintering from 915 to 980°C, pellet densities ranged from 90 to 96 % of theoretical, and similar superconducting properties were achieved. Critical current densities (J_c), measured in zero applied magnetic field at 77 K with a criterion of 1 μV/cm, were about 1000 A/cm^2 whereas samples prepared by the ambient-pressure method attain a value of only ~300 A/cm^2.

4. Conclusions

Solid-state reaction remains the simplest technique for synthesizing 123 superconductors. Use of $BaCO_3$, which is not hygroscopic, obviates the need for processing in carefully controlled humidity. A single calcination at 800°C for 4 h in reduced total pressure of oxygen gives essentially phase-pure, orthorhombic 123 powders. The reaction temperature is about 100-150°C lower than that used in ambient-pressure calcination and the lower temperature results in finer particles. The powder production rate depends on capacity of vacuum pumps and furnace reaction chambers; because both of these can be large, the process described here can produce many kilograms of phase-pure, orthorhombic 123 per day.

Acknowledgments

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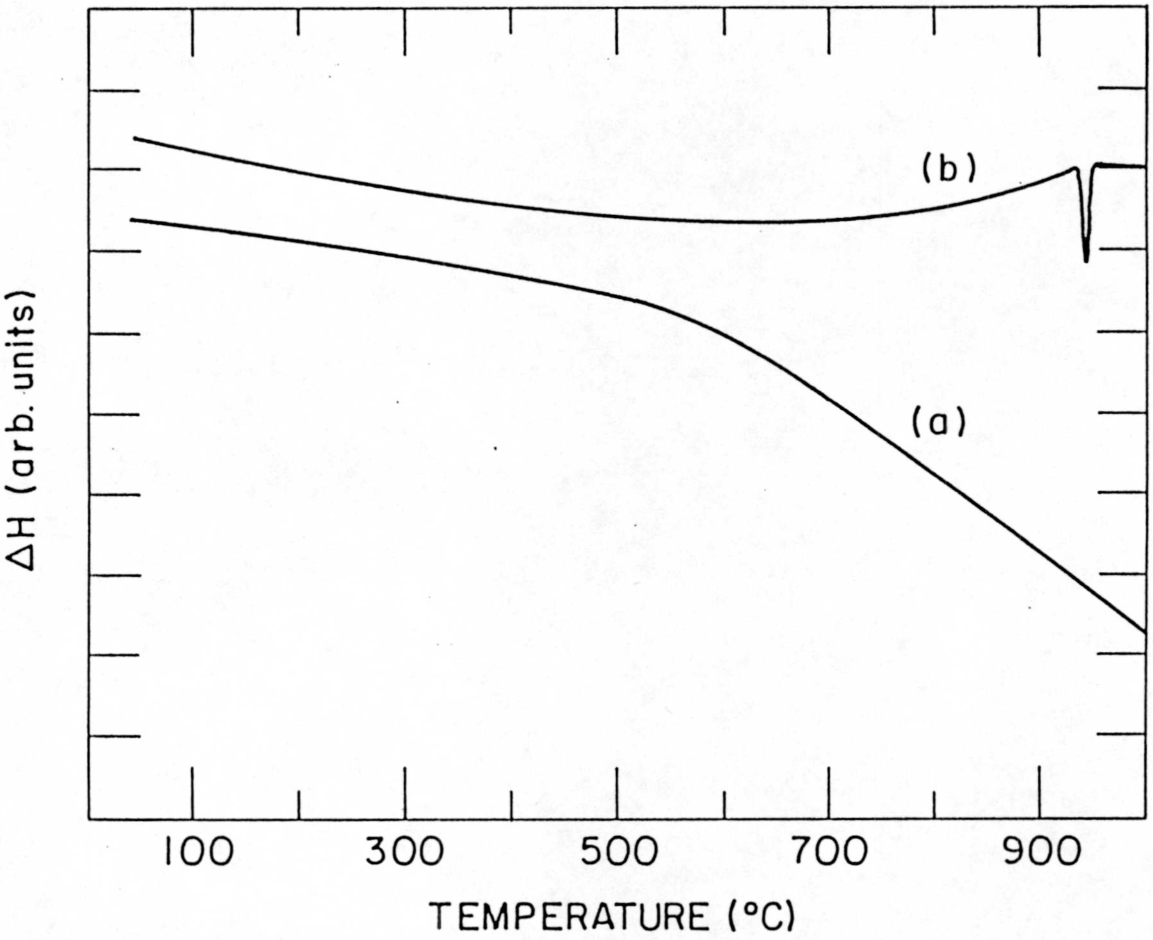
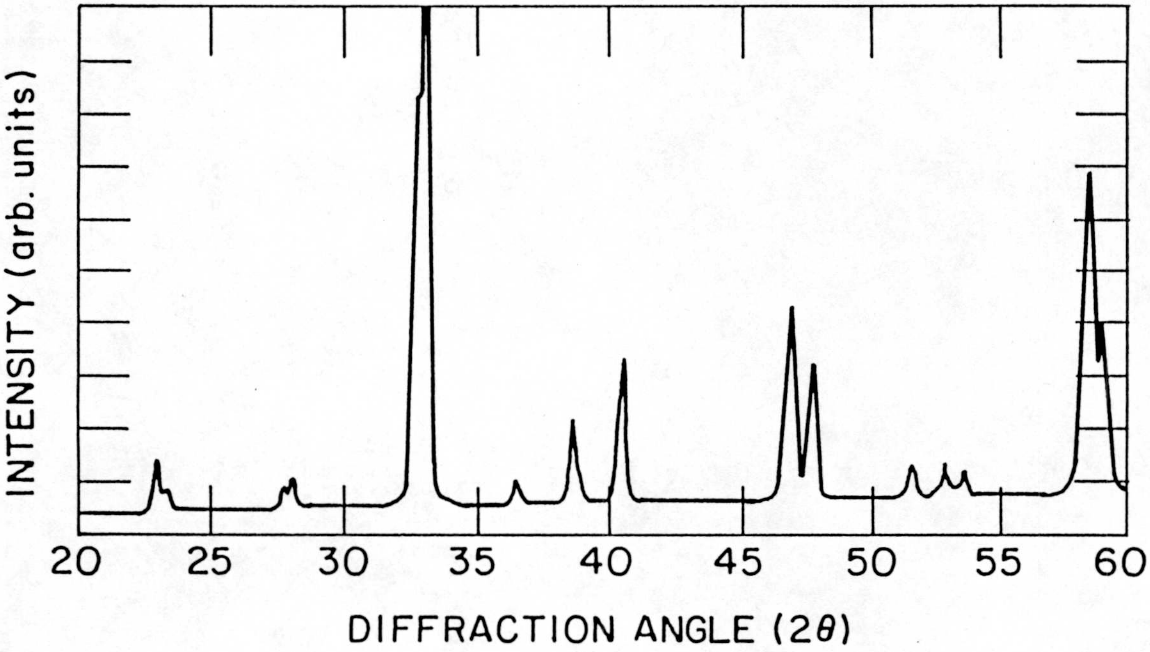
Figure captions

FIG. 1. Differential thermal analysis traces of 123 powder (a) calcined at 2 mm Hg pressure and (b) at ambient pressure.

FIG. 2. X-ray diffraction pattern of 123 powder prepared by low pressure calcination technique.


(b)
(a)
ΔH (arb. units)
100
300
500
700
900
TEMPERATURE (°C)


INTENSITY (arb. units)
20
25
30
35
40
45
50
55
60
DIFFRACTION ANGLE (2θ)