Synthesis of ceramic superconductors under low oxygen pressure

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Abstract. We have developed a process for synthesizing orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x$ (123) superconducting powders by calcination of the precursor powder under reduced total oxygen pressure. Because a single calcination at 800°C for 4 h in flowing oxygen at 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 $\sim 1000 \text{ A/cm}^2$ in zero applied magnetic field.

Keywords. Synthesis; improved calcination; ceramic superconductors.

1. Introduction

High-temperature ceramic superconductors are normally prepared via 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 . Also, the CO_2 released by decomposition of BaCO_3 can react with 123 to form BaCO_3 , Y_2O_3 , CuO and $\text{Y}_2\text{Cu}_2\text{O}_5$, depending on temperature (Fjellvag *et al* 1988). The presence of these nonsuperconducting phases, especially at grain boundaries, lowers critical current density (Shi *et al* 1988). In addition, the conventional 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; Lay 1989); in all cases, however, 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 $\sim 20^\circ\text{C/h}$ in the temperature range of 700–800°C in flowing O_2 at 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 CO_2 evolution 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 that during heating of the precursor powders at the ambient pressure of one atmosphere, the weight loss attributable to CO_2 evolution begins at about 750°C ; however, at 2 mm Hg, it begins at 620°C . Under reduced total pressure, decomposition is essentially complete at $\sim 800^\circ\text{C}$, whereas under ambient pressure, decomposition is not complete even at $\sim 1000^\circ\text{C}$. Heating of powders at $\sim 20^\circ\text{C}/\text{h}$ in the range of 700 – 800°C maintained CO_2 levels—as measured by FTIR—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 $\sim 2\%$ 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 (Goretta *et al* 1988). As shown in figure 1, for the powder calcined once at 800°C in low pressure, the only observed event 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 $\sim 940^\circ\text{C}$ caused by melting of a CuO - BaCuO_2 eutectic (curve b). These 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 (figure 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 $4\ \mu\text{m}$. 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.

Figure 1. Differential thermal analysis traces of 123 powder calcined at (a) 2 mmHg pressure and (b) ambient pressure.

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

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 at 915 to 980°C, pellet densities ranged from 90 to 96% of theoretical, and similar superconducting properties were achieved. Critical current densities, measured in zero applied magnetic field at 77 K with a criterion of $1 \mu V/cm$, were about $1000 A/cm^2$, whereas samples prepared by the ambient-pressure method attain a value of only about $300 A/cm^2$.

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 oxygen pressure 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 the capacities 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.

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