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Synthesis of a phase-pure orthorhombic $YBa_2Cu_3O_x$ under low oxygen pressure ☆

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Abstract

Reaction of Y_2O_3, $BaCo_3$ and CuO for 4 h at 800 °C in flowing O_2 with a total pressure of about 2.7×10^2 Pa, followed by cooling in O_2 at ambient pressure, has produced phase-pure orthorhombic $YBa_2Cu_3O_x$. Keeping the ratio of O_2 to evolved CO_2 above 50 was necessary to ensure phase purity. The resultant powder yielded pressed and inserted pellets with improved superconducting properties.

1. Introduction

High temperature ceramic superconductors are normally prepared by solid-state reaction of oxides, carbonates , or nitrates. For $Yba_2Cu_3O_x$ (YBCO), the mixed precursors are calcined at 890–980 °C for 20–100 h. Intermittent grinding is necessary to obtain relatively phase pure and homogeneous YBCO powders [1–4]. The high temperatures used in the conventional method can induce formation of liquids and non-superconducting phases such Y_2BaCuO_5 and $BaCuO_2$ [1]. The presence of these non-superconducting phases, especially at grain boundaries, lowers critical current density (J_c) [5]. In addition to producing undesirable phases, the conventional processes are time consuming and produce coarse particles.

By itself , $BaCO_3$, decomposes in ambient air at 1450 °C [6]; however, in the presence of yttrium and copper oxides, it decomposes near 800 °C. During calcination of the YBCO precursor, simultaneous decomposition of $BaCO_3$ and reaction among the three constituent oxides forms the desired perovskite phase. The CO_2 released by decomposition of $BaCO_3$ can, however, react with YBCO to form $BaCO_3$, Y_2O_3 and CuO, and $Y_2Cu_2O_5$, depending on temperature [7,8]. Kingon et al. [9] have also suggested that Ba-Cu-C oxide forms when YBCO is exposed to CO_2. Partial vacuums have been utilized by other investigators to calcine powders and to sinter polycrystalline bodies[10–12]; however, in all cases multiphase materials were obtained. We report here a synthesis route to obtain a phase-pure orthorhombic YBCO powders at 800 °C in flowing O_2 at reduced pressure.

2. Experimental Methods

Appropriate amounts of Y_2O_3, $BaCO_3$, and CuO were mixed as a 400 g batch and wet milled for 15 h in methnol in polyethylene jars containing ZrO_2 grinding media. The resultant slurry was pan dried and screened through a 30 mesh sieve. The screened powder was calcined for 4 h in flowing O_2 with a pressure of 2–20 mm Hg at a temperature of 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 Bomen Michelson 100 Fourier transform infrared (FTIR) spectrophotometer with 4 cm^{-1} resolution was used to monitor the evolution of CO_2 during calcination. Background spectra were recorded regularly between monitoring of the calcination process. Heating and O_2 flow rates were adjusted to maintain various levels of CO_2 during calcination.

3. Results and discussion

As shown in Fig. 1, the weight loss attribute to CO_2 evolution during heating the precursor powders begins at about 750 °C at the

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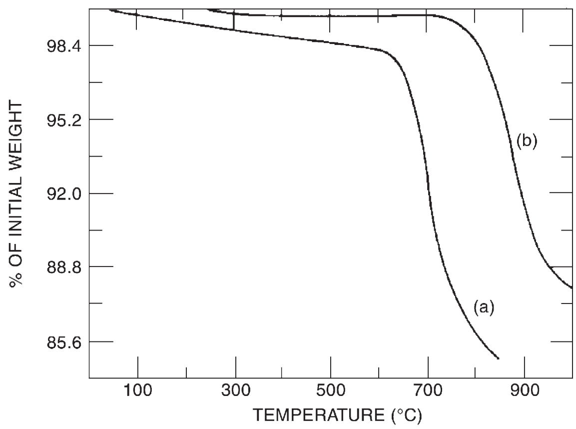

Fig. 1. Change in mass observed by thermogravimetric analysis during heating of YBCO precursor powders: (a) pressure of 2.7×10^2 Pa; (b) ambient pressure.

ambient pressure of 1×10^5 Pa (curve b); it begins at about 620 °C, however, at 2.7×10^2 Pa (curve a). More weight was lost from the low-pressure mixture because additional O_2 was also liberated. Heating powders at less than 20 °C in 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 O_2. Faster heating rates resulted in higher CO_2 concentrations and yielded powders containing Y_2BaCuO_5 and other impurity phases. The best powders were obtained when the total pressure was maintained at 2.7×10^2 Pa. Endothermic or exothermic reactions or melting events associated with impurity phases were identified by differential thermal analysis [1]. For the powder calcined at low pressure, the only event observed was a change in slope caused by conversion of the powder from orthorhombic to tetragonal upon heating (Fig. 2). Conventionally processed powder exhibited an endotherm at about 920 °C, caused by melting of a $CuOBaCuO_2$ eutectic [13].

The YBCO powder was processed at 2.7×10^2 Pa was also shown to be the phase pure by X-ray diffraction. Analysis of the orthorhombic-peak split and comparison against published data [14] revealed that no tetragonal phase was present in the powder. The splitting of the (123) and (213) peaks is shown in Fig. 3.

The particle size of the powder resulting from 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 890 °C or greater,because diffusional kinetics in YBCO are faster in reduced O_2 pressures [15,16]. A partial vacuum

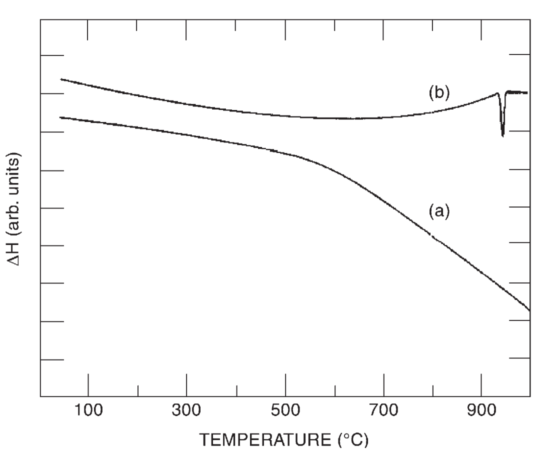

Fig. 2. Differential thermal analysis traces of YBCO powder (a) calcined at 2.7×10^2 Pa and (b) at ambient pressure.

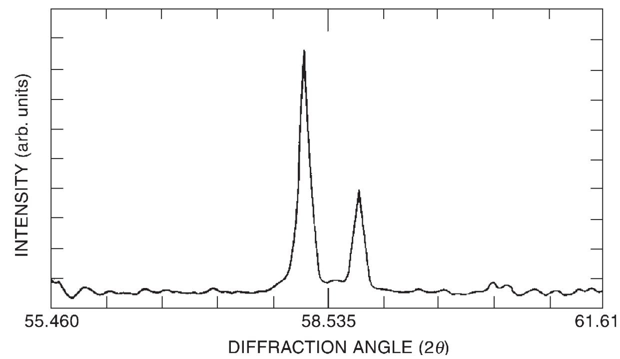

Fig. 3. X-ray diffraction pattern of YBCO synthesized at 2.7×10^2 Pa and cooled in O_2, showing (123) and (213) peaks.

was used, instead of a mixture of O_2 and noble gas, because CO_2 was removed in with increased efficiency. A phase-pure powder was synthesized after only 4 h at 800 °C in O_2 at a pressure of 2.7×10^2 Pa. The absence of other phases may be attributed, in part to rapid reaction kinetics; however, it must also indicate the inherent stability of the $Yba_2Cu_3O_x$ phase under the processing conditions.

The resultant YBCO 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. The critical current densities (J_c), measured in zero field at 77 K with a criterion of 1 μV/cm, were about 1.0×10^3 A/cm^2. Furthermore, it is generally found that the best high-temperature superconductors also have the best metallic behavior. The lowest resistivity at onset of superconductivity [5]obtained was less than 100 μΩ cm, and the highest ratio of room-temperature resistivity to that at onset of superconductivity was greater than 7. Both values represent a two-fold improvement over conventionally processed powders. Since the microstructures of pressed and sintered pellets are non-uniform and only slightly textured, the limits in J_c that are inherent in powder processed in reduced O_2 pressure have yet to be identified.

Solid-state reaction remains the simplest technique for synthesizing YBCO. Use of $BaCO_3$, which is not hygroscopic, obviates the need for processing in carefully controlled humidity. Reaction at the relativity low temperature of 800 °C can be carried out in flowing O_2 of reduced pressure. If CO_2 levels are kept sufficiently low, phase-pure YBCO is obtained. Since vacuum pumps and reaction chambers can be quite large, the process can produce many kilograms of YBCO per day.

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