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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 mm Hg, followed by cooling in O_2 at ambient pressure, has produced phase-pure orthorhombic $YBa_2Cu_3O_x$ (123). During calcination, $BaCO_3$ first decomposes and then reacts to form intermediate compounds. Reactions among the intermediate compounds result in formation of the 123 superconductor. Formation of intermediate compounds during calcination was monitored by X-ray diffraction, scanning electron microscopy, and thermal analyses of precursor powders heated to various temperatures up to 800°C. The reaction passes through the formation of $BaCuO_2$, $BaCO_3$, $Y_2Cu_2O_5$, and Y_2BaCuO_5. The123 phase begins to form at temperatures as low as 725°C in a pressure of about 2 mm Hg of oxygen.

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 in ambient pressure air or O_2 at 900-950°C for 50-100 h with intermittent grindings [1]. The high calcination temperatures used in the conventional method result in the formation of liquid phases and some nonsuperconducting phases such as Y_2BaCuO_5 (211), $BaCO_3$, and $BaCuO_2$. Multiple calcination with intermittent grinding is used to promote homogenization of the powder. Keating et al. [2] identified eight phases during calcination of the precursor mixtures in the temperature range from 625 to 975°C. The temperature at which the 123 phase forms depends upon the type of precursor and atmosphere used during processing. Horowitz et al. [3], using a variety of sol-gel precursors, reported the formation of the 123 phase below 725°C in an inert environment. Thin films of 123 have been fabricated at processing temperatures below 635°C [4].

Kinetics of the reactions and reaction pathways that lead to the formation of 123 in ambient pressure were investigated by Ruckenstein et al. [5]. Analyzing air-quenched samples with X-ray diffraction, they found that decomposition of $BaCO_3$ is the rate-limiting step. Gadalla and Hegg [6] used thermal analyses to study the kinetics of the solid state reaction of $BaCO_3$, Y_2O_3, and CuO in air and concluded that six overlapping steps occurred during formation of 123. Thomson et al. [7] reported on the reaction sequences that lead to the formation of the 123 from two different precursors and under helium and air environments. In air, the reactants in both precursor systems produced an intermediate 123 phase at 725°C without going through the $BaCuO_2$ and Y_2BaCuO_5 intermediate phases. In helium, the fully developed 123 tetragonal phase was formed at temperatures as low as 600°C, but it also decomposed to $BaCu_2O_2$, $BaCuO_2$, and Y_2BaCuO_5. In all of the previous studies the reaction sequences were studied either in an inert atmosphere, air, or oxygen at ambient pressures. Under these conditions, the CO_2 released by decomposition of $BaCO_3$ during calcination can react with 123 to form $BaCO_3$, Y_2O_3, CuO, $Y_2Cu_2O_5$, and $BaCuO_2$, depending on the temperature [8-14]. Therefore, in ambient pressure conditions, one can not separate the contribution of the CO_2-related decomposition products from the actual intermediate phases in the reaction between oxides of yttrium, barium, and copper. In the present work, we have studied the formation of intermediate phases without the interference from the CO_2-related decomposition products. The CO_2 generated during the decomposition of $BaCO_3$ is removed effectively by a partial vacuum during the calcination of the precursor [15].

Experimental

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 in flowing O_2 at a pressure of ≈2 mm Hg in the range 725-800°C. The heating rate and time at peak temperatures were varied. During cooling, the vacuum was discontinued and ambient pressure O_2 was passed. A 3-h hold at ≈500°C was incorporated into the cooling schedule to promote oxygenation of the resulting powder. The calcined powders were characterized by thermal analyses and X-ray diffraction. The powders were also cold pressed at 140 MPa and sintered at 900°C in ambient pressure atmosphere containing 1% O_2/99% N_2 gas mixture. The microstructures of sintered samples were analyzed by optical microscopy.

Results and Discussion

Thermogravimetric analysis (TGA) showed that during heating of the precursor powders at the ambient pressure of one atmosphere, the weight loss attributed 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 ≈800°C, whereas under ambient pressure, decomposition is not complete even at ≈1000°C [15]. Heating of powders at ≈20°C/h in the range of 700-800°C maintained CO_2 levels 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% in the oxygen atmosphere [8]. 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) [1]. Figure 1 shows the DTA traces of 123 precursor powders calcined at ambient pressure in air at 925°C a) once, b) twice, and c) three times. The powders were ground and mixed between each calcination. In all three DTA traces, as seen from Fig. 1, two endotherms are present, one with onset at ≈940°C and another at ≈1020°C. The endotherm with onset at ≈1020°C corresponds to incongruent melting of 123 phase. The ternary peritectic reaction, $YBa_2Cu_3O_x + CuO \rightarrow Y_2BaCuO_5$ + liquid, is responsible for the partial melting at ≈940°C [16]. In addition, a ternary eutectic between $BaCuO_2$,CuO, and 123 can form a molten phase at about 930°C [17]. The relative intensity of the endotherm at ≈940°C, due to presence of impurity phases, in the calcined powder decreased as the number of intermittent calcination steps increased, but it was present even after three repeated calcinations in ambient pressure. This endotherm is due to decomposition products formed by reaction of 123 with CO_2 at the calcination temperature [9,10]. In the absence of CO_2-effect, any $BaCuO_2$ formed as intermediate phase will react with rest of the material and form 123 at ≈800°C [15]. In the reduced total pressure calcination technique, the CO_2 evolved is removed effectively and the level of CO_2 in the calcining atmosphere is maintained below about 2% - level above which 123 decomposes into undesired non-superconducting phases. The DTA trace shown in Fig. 2 for 123 prepared by reduced pressure calcination at 800°C for 4 h in flowing O_2 is free from the endotherm at ≈940°C. The only observed event is a change in slope caused by conversion of the powder from orthorhombic to tetragonal upon heating.

The 123 powder processed at low pressure was also shown to be phase-pure by X-ray diffraction (Fig. 3). Analysis of the orthorhombic-peak split and comparison against published data [18] 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 [19]. A partial vacuum was used instead of a mixture of O_2 and a noble gas because CO_2 was removed with increased efficiency.

Intermediate phase formation was monitored by heating the precursors to various temperatures in flowing O_2 at a pressure of $\approx$2 mm Hg. X-ray diffraction indicated $BaCO_3$, $BaCuO_2$, and CuO as major phases and 211, $Y_2Cu_2O_5$, Y_2O_3 as minor phases in the powder heated up to 725°C and cooled. No 123 was detected, within the limitation of the equipment used, in this powder. Trace amounts of 123 were present when the precursor powders are held at 725°C for 10 h in $\approx$2 mm Hg pressure. In addition to $BaCuO_2$, $BaCO_3$ and CuO, Y_2O_3 also appeared as major phase when the temperature was increased to 730°C. In the sample cooled as soon as it reached 730°C, 123 was not detected; however, minor amounts of 123 developed when held at 730°C for 10 h. The amounts of 123 in the powder increased as the temperature was raised to 800°C. $BaCuO_2$ and $BaCO_3$ were present in small quantities even in samples heated to 800°C and cooled. Figure 4 shows the optical micrograph of a sample sintered at 900°C in ambient pressure. In addition to impurity phases, a large amount of porosity within the grains, possibly due to trapped CO_2, is evident from Fig. 4. Complete conversion of the powder into 123 occurs only if the precursors were held at 800°C for about 4 h in ≈2 mm Hg pressure. Pellets pressed from this powder and sintered at 900°C for 10 h in ambient pressure exhibited ≈94% of theoretical density and were free from secondary phases.

Ruckensten et al. [5] and Gadalla and Hegg [6] concluded that the reaction series leading to the formation of the 123 are diffusional controlled, with $BaCuO_2$, $Y_2Cu_2O_5$ and 211 as intermediate phases. When Y_2O_3, $BaCO_3$, and CuO mixtures were calcined at 940°C in ambient pressure conditions [5], initially $BaCO_3$ decomposed rapidly, but later the reaction rate slowed. This occurs because the diffusion of CO_2 is limited at ambient pressure by the formation of 123 and $BaCuO_2$ at the surfaces. The activity of CO_2 in the atmosphere surrounding the samples is high and causes the 123 to decompose. In the present study, a reduced total pressure was used, and the CO_2 generated was removed effectively and, therefore, no $BaCuO_2$, $Y_2Cu_2O_5$ or 211 phases are present when calcined at 800°C for 4 h in 2 mm Hg pressure (Fig. 2). It should be noted that Thomson et al. [7], using citrate and flashed nitrate gel precursors, showed by in-situ X-ray diffraction that tetragonal 123 formed as intermediate phase at 725°C. They did not observe any evidence of 211 as intermediate phase in either precursor. The reaction path is influenced by the interparticle diffusion and in the gel precursors, the reactants were mixed on a nanometer scale, thus the effects of interparticle diffusion are minimized. The diffusion lengths are longer in the mixed oxide/carbonate precursors and therefore leads to formation of 211, $BaCuO_2$, $Y_2Cu_2O_5$, etc. as intermediate phases. Even though solid state reaction of mixed oxides and carbonates was used in the present study, the O_2 pressure was kept low (≈2 mm Hg) and the intermediate phases reacted, due to enhanced diffusivity of cations at low pressures, and transformed into 123 at 800°C. In the previous work [5], since ambient pressure was employed, CO_2-induced decomposition products were present even after heating at 940°C. Our observation, by X-ray diffraction, of the the presence of 123 as minor phase in powders heated for 10 h at 725°C in reduced pressure is in agreement with the results of Thomson et al. [7] using gel precursors.

Conclusions

$Y_2Cu_2O_5$, $BaCuO_2$, $BaCO_3$, and 211 were formed as intermediate phases when the precursors were heated in flowing O_2 at a pressure of ≈2 mm Hg. Reaction among the intermediate phases resulted in formation of the 123 at temperatures ≈725°C. Fully reacted single phase 123 was formed by heating at ≈800°C for 4 h. This was possible owing to increased diffusivity of cations in reduced O_2 pressure. In the conventional, ambient pressure processing, these intermediate phases remained even after 10 h of calcination at ≈950°C.

Acknowledgment

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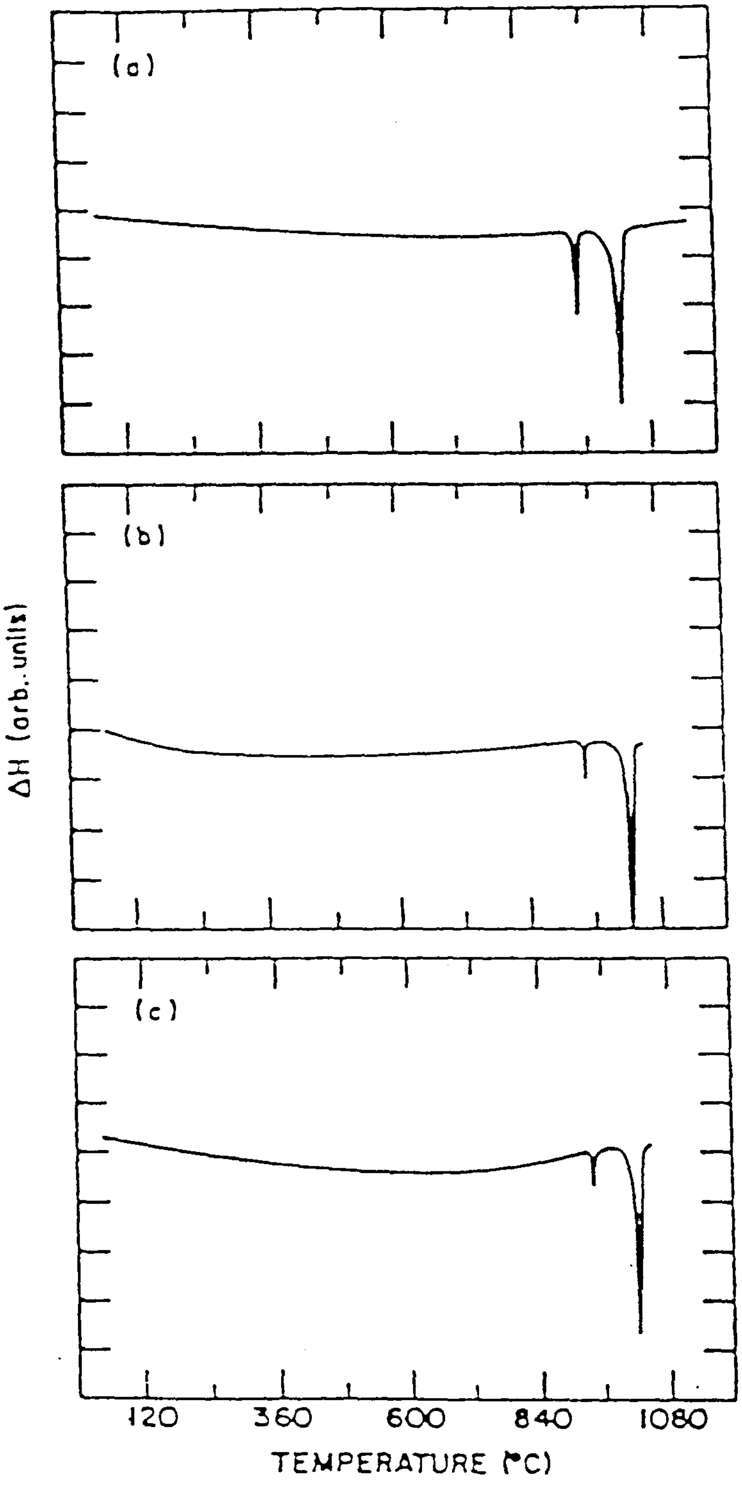
Figure captions

Figure 1. DTA traces of 123 precursor heated in ambient pressure at 925°C: a) once, b) twice, and C) three times.

Figure 2. DTA trace of 123 powder prepared by heating in flowing O2 at a pressure of 2 mm Hg for 4 h.

Figure 3. X-ray diffraction pattern of 123 powder prepared by low pressure calcination.

Figure 4. Optical micrograph of 123 containing $BaCuO_2$ and $BaCO_3$ impurity phases.



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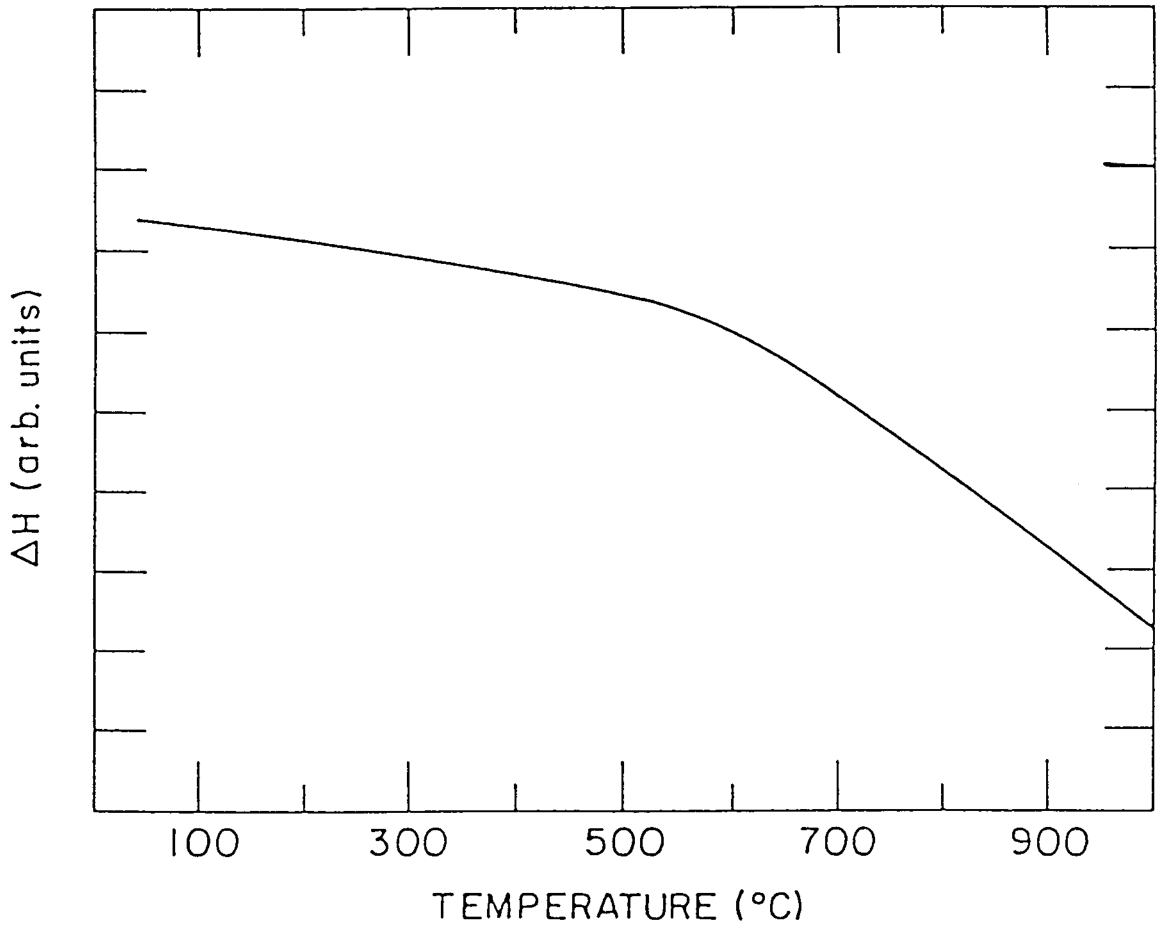
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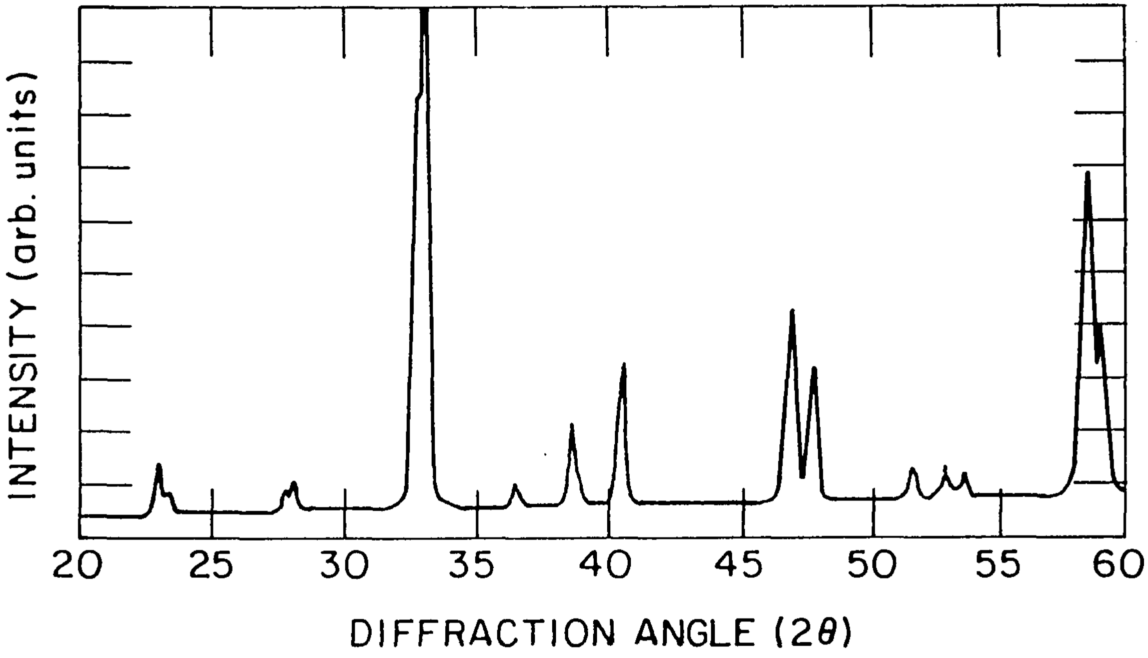
700
900
TEMPERATURE (°C)



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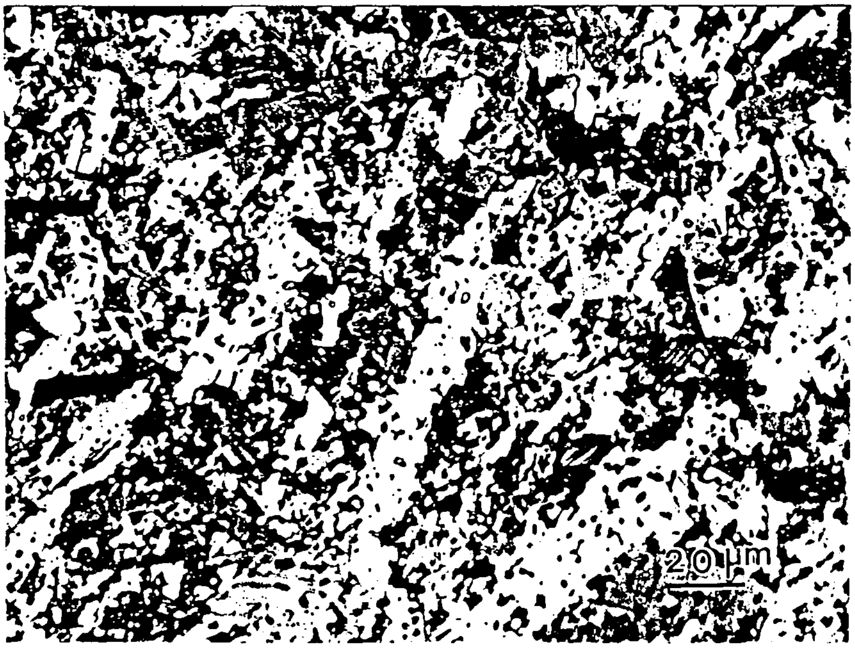
30
35
40
45
50
55
60
DIFFRACTION ANGLE (2θ)



4