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The $YBa_2Cu_3O_x$ (123) superconductor has been prepared by a new method using the ternary precursors $BaCuO_2$ and $Y_2Cu_2O_5$. The $BaCuO_2$ is prepared by calcining a mixture of $BaCO_3$ and CuO at a temperature of ≈850°C in flowing oxygen at reduced total pressure, followed by ambient-pressure heating at ≈925°C. The $Y_2Cu_2O_5$ is synthesized by a solid–state reaction between Y_2O_3 and CuO in ambient pressure at ≈950°C. A stoichiometric mixture of $BaCuO_2$ and $Y_2Cu_2O_5$ is heated to ≈950°C to form 123. The reaction between $Y_2Cu_2O_5$ and $BaCuO_2$ is very fast and results in nearly phase-pure 123 in a short period.

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 intermittent grinding is used to promote homogenization of the powder. Atmospheric contaminants such as CO_2, H_2O, and residual carbon strongly affect the transition temperature (T_c), critical current density (J_c), and width of the superconducting transition of $YBa_2Cu_3O_x$ (123) superconductors [2-7]. Barium carbonate ($BaCO_3$) is a commonly used barium source in bulk processing of 123. During calcination of the precursor, simultaneous decomposition of $BaCO_3$ and reaction among the three constituent oxides form 123. The CO_2 released by decomposition of $BaCO_3$ reacts with 123 and forms nonsuperconducting $BaCuO_2$, Y_2O_3, CuO, $Y_2Cu_2O_5$, and Y_2BaCuO_5 (211), depending on temperature [8]. The presence of these nonsuperconducting phases, especially at grain boundaries, lowers the J_c [9]. Heating the precursor that contains $BaCO_3$ either in flowing O_2 under a reduced total pressure (partial vacuum) or in an inert atmosphere enhances the decomposition of $BaCO_3$, minimizes the level of CO_2 in the atmosphere surrounding the powder, and improves the quality of superconductor [10-14].

Even though the quality of the superconductor powder produced by reduced–pressure calcination is improved over the conventionally processed material, these powders may have small amounts of retained carbon. Carbon has an appreciable solubility in 123 [2,4,5]. During synthesis, it is often necessary to hold the powders at temperatures ≈950°C or higher for long periods to remove the residual carbon. Higher temperatures result in the formation of liquid phases and some nonsuperconducting phases such as 211 and $BaCuO_2$.

Use of $BaCuO_2$, a carbon-free source of Ba, in the preparation of 123 will eliminate this problem. $BaCuO_2$ has been used by few investigators [15-17]. In all of the earlier studies, the $BaCuO_2$ was prepared either in ambient pressure air or O_2. Ruckenstein et al. [17] used small quantities (≈0.5 g) of $BaCuO_2$, $Y_2Cu_2O_5$, Y_2O_3, and CuO and studied the kinetics of the reaction leading to the formation of 123. In this work, we report a technique for synthesizing large quantities of 123 using $BaCuO_2$ and $Y_2Cu_2O_5$ as precursors. We have prepared $BaCuO_2$ by calcining a mixture of $BaCO_3$ and CuO in flowing O_2 in reduced total pressure to facilitate the removal of the evolved CO_2 from the system.

EXPERIMENTAL

Stoichiometric amounts of $BaCO_3$ and CuO to form ≈400 g of $BaCuO_2$ were wet-milled for ≈20 h in methanol using ZrO_2

grinding media. The resultant slurry was pan-dried in air, ground in an agate mortar, heated to ≈850°C in flowing O_2 at a pressure of ≈2 mm Hg, and held for 24-h. The vacuum was discontinued after the 24 h hold at ≈850°C, ambient-pressure O_2 was passed over the powder, and the temperature was raised to ≈925°C for 12 h. This calcination procedure, as determined by X-ray diffraction (XRD) and differential thermal analysis (DTA), resulted in phase-pure $BaCuO_2$.

To obtain ≈400 g of $Y_2Cu_2O_5$, stoichiometric amounts of Y_2O_3 and CuO were mixed as above and heated in flowing O_2 at ambient pressure to ≈980°C for 20 h. The phase purity of the $Y_2Cu_2O_5$ was confirmed by XRD and DTA. Stoichiometric amounts of $BaCuO_2$ and $Y_2Cu_2O_5$ were mixed and heated to ≈950°C in ambient-pressure O_2 for times ranging 5 to 70 h. The reacted powder was characterized by XRD, DTA, and optical and scanning electron microscopy. Reactions between $BaCuO_2$ and $Y_2Cu_2O_5$ were monitored by thermal analysis at a heating rate of 3°C/min in ambient-pressure O_2.

RESULTS AND DISCUSSION

In Fig. 1, curve (a) shows the weight change measured by thermogravimetric analysis (TGA) while heating stoichiometric amounts of $BaCuO_2$ and $Y_2Cu_2O_5$ in ambient-pressure O_2. For comparison, the TGA trace obtained in heating a mixture of Y_2O_3, $BaCO_3$, and CuO is shown by curve (b). The total weight loss observed while heating $BaCuO_2$ and $Y_2Cu_2O_5$ precursor to ≈1000°C was ≈1.3%; onset of this weight loss, as seen in Fig. 1a, occurs at ≈940°C. $BaCuO_2$ and $Y_2Cu_2O_5$ react and form 123 at ≈940°C [16,17]. The value of x in $YBa_2Cu_3O_x$ is measured as 6.35 at 950°C in ambient-pressure O_2 [18]. Therefore, the small observed weight loss shown by curve (a) is due to loss of O_2 from the 123 phase at these high temperatures. The 123 powder processed from the $BaCuO_2$ and $Y_2Cu_2O_5$ precursors was shown to be phase-pure by XRD.

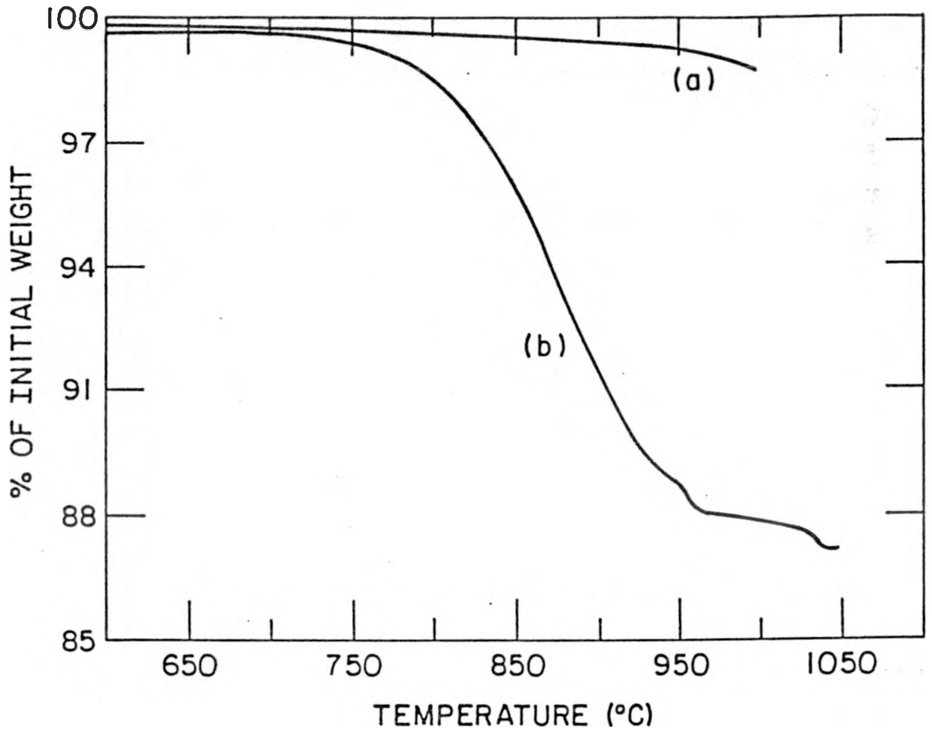

Figure 1 Change in mass observed by thermogravimetric analysis during ambient-pressure heating of precursors: (a) $BaCuO_2$ and $Y_2Cu_2O_5$ mixture; (b) Y_2O_3, $BaCO_3$, and CuO mixture.

For mixed precursors containing Y_2O_3, $BaCO_3$, and CuO, as seen from curve (b), the weight loss attributable to CO_2 evolution begins at ≈750°C; the total weight loss measured in this precursor is ≈13%. The powder mixture turned into a hard cake upon cooling from ≈1000°C. There was a color gradient from the surface (black) to the center (greenish) of the hard cake. XRD indicated the surface to be 123, whereas the core contained 211 and $BaCuO_2$, as well as minor amounts of 123. During ambient-pressure heating of the precursors that contains $BaCO_3$, the removal of evolved CO_2 from core regions is severely limited, especially by the formation of 123 at the surface. The partial pressure of CO_2 in the core region may exceed the thermodynamically calculated equilibrium value and cause decomposition reactions. At 900°C in O_2 under ambient pressure, the equilibrium partial pressure of CO_2 at which 123 becomes unstable is ≈2% [8]. Because each gram of Y_2O_3, $BaCO_3$, and CuO precursor mixture evolves ≈0.25 L of CO_2, it is conceivable that the local CO_2 partial pressure in the core region exceeded this limit and resulted in 211 and $BaCuO_2$.

Endothermic or exothermic reactions, i.e., melting events, associated with impurity phases were identified by DTA [1]. In Fig, 2, curve (a) shows the DTA traces obtained while mixtures of $BaCuO_2$ and $Y_2Cu_2O_5$ are heated. The only observed event was an endotherm with an onset at ≈1015°C. According to available phase diagrams [19,20], 123 is the only compound between $BaCuO_2$ and $Y_2Cu_2O_5$. Therefore, the endotherm in curve (a) is due to peritectic melting of 123. XRD on powder heated to 1025°C and cooled revealed the presence of 123, 211, $BaCuO_2$, and CuO. These phases were formed as a result of the peritectic reaction. XRD of large batches (≈200 g) of powders obtained by heating $BaCuO_2$ and $Y_2Cu_2O_5$ at ≈950°C for 5 h in ambient-pressure O_2 showed phase-pure 123 with no secondary phases. No changes were detected by heating the powder mixtures for longer times.

The DTA trace obtained by heating the precursor that contains Y_2O_3, $BaCO_3$, and CuO is shown by curve (b) of Fig. 2. There are three endotherms present in this DTA trace. The endotherm with onset at ≈850°C represents the transformation of γ-$BaCO_3$ to the hexagonal β-form [6,21]. The formation of a liquid phase in compositions along the 123–CuO join has been investigated by Aselage and Keefer [21]. They observed the onset of melting in 123–CuO at ≈940°C. $BaCuO_2$ and 211 were detected in addition to 123 and CuO in the melted and cooled samples, indicating the endotherm at ≈940°C is not a simple eutectic. A eutectic melting will result in 123 and CuO in the cooled sample. Therefore, the endotherm with onset at ≈940°C in curve (b) is due to a ternary peritectic reaction between 123 and CuO that forms 211 and liquid. The endotherm with onset at ≈1015°C is, of course, the result of incongruent melting of 123 to 211 plus a

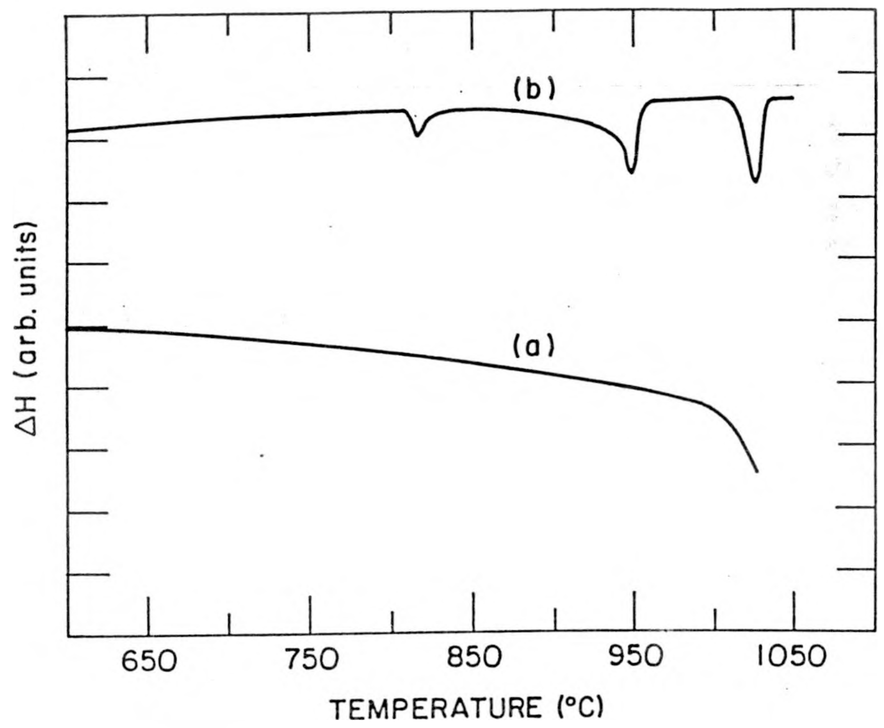

Figure 2 Differential thermal analysis traces during ambient-pressure heating of precursors: (a) $BaCuO_2$ and $Y_2Cu_2O_5$ mixture; (b) Y_2O_3, $BaCO_3$, and CuO mixture.

liquid. From Fig. 2, we see that when Y_2O_3, $BaCO_3$, and CuO mixtures are heated, the result is several intermediate compounds and transient melts in addition to 123.

Ruckenstein et al. [17] reported that the reaction among Y_2O_3, $BaCO_3$, and CuO was initially very fast but slowed considerably after about 20 min at 940°C in ambient pressure. $Y_2Cu_2O_5$, $BaCuO_2$, and 211 were observed as intermediate phases. To achieve homogeneity and phase purity, the Y_2O_3, $BaCO_3$, and CuO precursor mixtures are subjected to multiple calcination in ambient pressure at 900-950°C for 50-100 h with intermittent mixing and grinding. Long calcination times and high temperatures lead to larger particle sizes and wide particle-size distributions. 123 prepared by calcining mixtures of Y_2O_3, $BaCO_3$, and CuO four times at ≈925°C in ambient-pressure conditions exhibit the endotherm with onset at ≈940°C, which is caused by peritectic melting of 123 and CuO [10]. As mentioned earlier, one way to avoid this problem is to use a partial vacuum during calcination of precursors that contain carbonates [10-14]. An alternate technique, as shown in this work, is to use $BaCuO_2$ and $Y_2Cu_2O_5$ as precursors and to process in ambient-pressure condition. Ruckenstein et al. [17] used $BaCuO_2$ and $Y_2Cu_2O_5$ and studied the reaction kinetics, but the sample sizes were ≈0.5 g. In the present study, we have shown that large batches of phase-pure 123 can be formed by using $BaCuO_2$ and $Y_2Cu_2O_5$ as precursors. Both react very rapidly at ≈950°C in ambient-pressure oxygen, and no intermittent mixing or multiple calcinations are needed.

CONCLUSIONS

Phase-pure 123 superconductor has been prepared by heating the ternary precursors $BaCuO_2$ and $Y_2Cu_2O_5$ in ambient-pressure oxygen at ≈950°C. $BaCuO_2$, which is difficult to synthesize under ambient-pressure conditions, is easily prepared in phase-pure form in flowing O_2 under reduced total pressure. $Y_2Cu_2O_5$ is synthesized by a solid–state reaction between Y_2O_3 and CuO in ambient-pressure at ≈950°C. The reaction between $BaCuO_2$ and $Y_2Cu_2O_5$ is very rapid and forms 123 without the additional formation of intermediate compounds or transient liquids. The electrical properties of sintered pellets made from this 123 powder are currently under investigation.

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