Preparation and characterization of $YBa_2Cu_3O_{7-x}$ superconductor by means of a novel method combining sol–gel and combustion synthesis techniques

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Since the discovery of $YBa_2Cu_3O_{7-x}$ (Y123) by Wu *et al.* in 1987 [1, 2], the applications of high-T_c ceramic superconductors in scientific and engineering fields have been increasing continuously [3–5]. The conventional method of preparing Y123 powders is by the solid-state reaction of oxides and carbonates [1, 2, 6]. These starting materials are stoichiometrically mixed, and then calcined in air or oxygen at atmospheric pressure and a temperature of 900–980 °C for 20–50 hr. Intermittent grinding is required to obtain phase-pure and homogeneous Y123 powders. Although the method is relatively simple, and alternative processes exist which decrease the total reaction time [7], all of the conventional solid reaction processes are, in general, time-consuming and energy-intensive. Recently, a variety of wet-chemical synthesis methods have also been reported to be effective in generating ultrafine and more homogeneous powders of ceramic oxides [8–10]. Relatively complex schedules and low production rates are the common problems of the wet-chemical methods. Fortunately, the drawbacks of these methods as mentioned above could be partially eliminated by the combustion synthesis method, which has been applied to the synthesis of various high performance materials including ceramics, intermetallics, and composites [11, 12]. Among its many advantages are low processing cost, and high energy efficiency and production rates [13]. However, the lack of homogeneity and relatively lower purity of the synthesized product are two potential disadvantages.

Recently, several researchers have used a sol–gel combustion method to synthesize ferrite and perovskite powders [14–16]. This is a novel and unique technique that combines the chemical sol–gel process and the combustion synthesis process. The advantages of this technique include inexpensive precursors, simple preparation process, and a resulting submicron-sized powder with high homogeneity. Although there have been some investigations in which various ceramic oxides were synthesized by this method, no information is available on the synthesis of Y123 using this method. Hence, this work attempts to synthesize Y123 powder by means of the combustion synthesis of the dried gel obtained from metal nitrates and citric acid.

Y123 superconductor was prepared according to the procedure shown in Fig. 1. Analytical-grade yttrium nitrate, barium nitrate, copper nitrate, and citric acid were used as raw materials. Appropriate amounts of metal nitrates and citric acid, in order to form 25 g of Y123 powder, were first dissolved in 400 ml of distilled water. A small amount of ammonia was added to the solution to adjust the pH value to about 7. During the procedure, the solution was stirred vigorously using a magnetic agitator. The neutralized solution was stirred continuously and thoroughly evaporated by heating on a hot plate to transform it into a dried gel. When ignited in air, the dried gel burnt and a loose product (will be referred to as "as-burnt powder") was formed. Then, the as-burnt powder was calcined at 900 °C for 12 hr. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the dried gel were carried out at a heating rate of 10 °C/min in static air using a thermal analyzer (Seiko SSC 5000, Japan). Infrared spectra (IR) for the dried gel and the as-burnt powder were recorded on a spectrophotometer (Bomen DA8.3, Canada) from 500 to 4000 cm^{-1} by the KBr pellet method. The calcined powder was put under a pressure of ∼250 MPa into a 25-mm diameter and 5-mm thick disc, which was then sintered at 930 °C for 6 hr in air and slowly cooled to room temperature. The disc, after the sintering process, is hereafter referred to as the "sintered body." The phase identification of the samples at different stages of the process was performed using X-ray diffraction (XRD) (Siemens D5000, Germany) with Cu K_α radiation. The morphology of the as-burnt and the calcined powders were observed using a scanning electron

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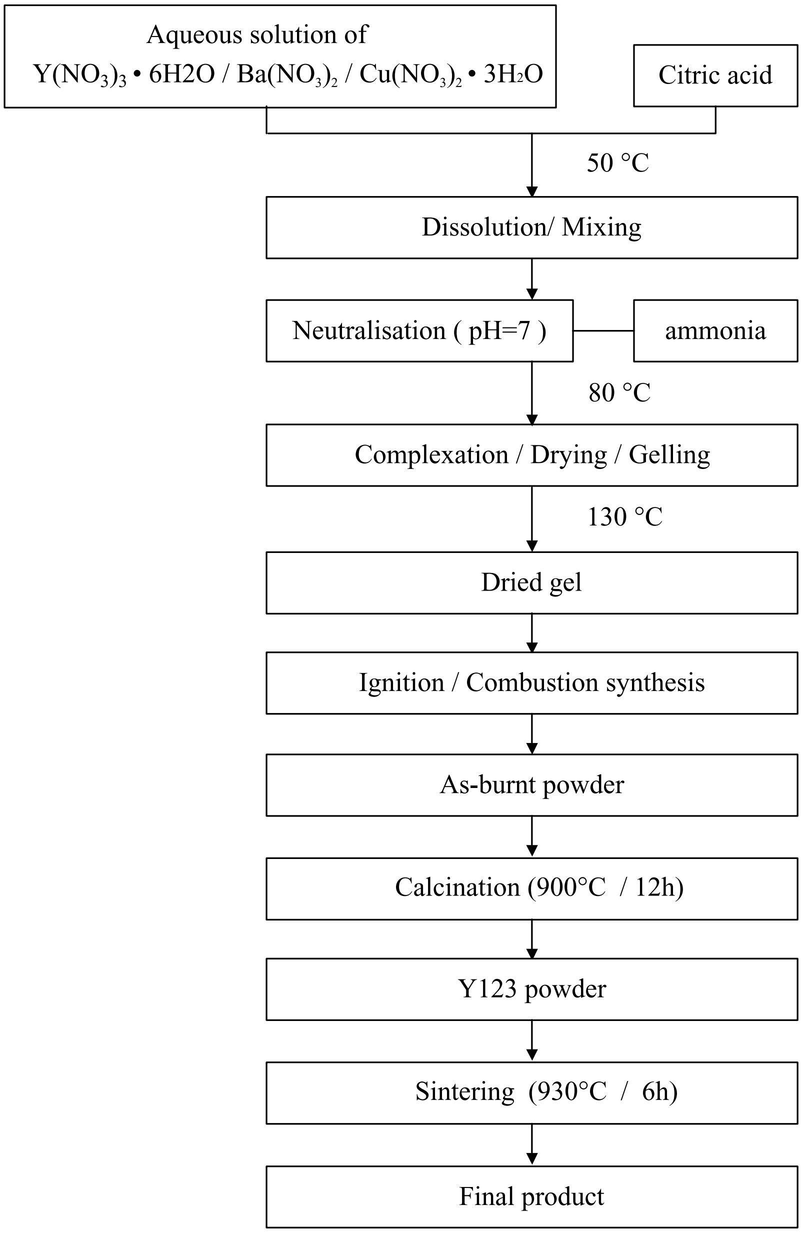

Figure 1 Preparation procedure of Y123 superconductor by the sol–gel/combustion synthesis method.

microscope (SEM) (Jeol-JSM840A, Japan). The electrical resistance was measured by the standard four-probe technique, wherein Pt wires were attached to the sample using silver paste, and the temperature was determined with a calibrated silicon diode sensor. The magnetic property of the calcined powder was examined with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPNS7, USA). Liquid nitrogen and an Nd–Fe–B magnet were used to examine the Meissner effect of the sintered body.

On the basis of the experimental observation, it was found that the dried gel exhibited a self-propagating combustion behavior (see Fig. 2). When the dried gel was ignited, the combustion propagated forward until all dried gel was completely burnt out, forming a loose powder appearing gray-brown in color. The combustion front velocity was approximately 4 mm/s by visual observation. It was also found that a light-brown gas with a pungent smell was released during the combustion reaction. The gas was identified as the mixture of NO_x, CO, and CO_2 by escaping gas analysis (EGA).

TGA–DTA results for the dried gel are given in Fig. 3, which shows a sharp exothermic peak at ~230 °C with a concurrent weight loss of 80%. Thermal analysis results suggest that the dried gel decomposes exothermically in a single step at about 230 °C, which may be caused by the reaction of nitrates and citric acid.

Fig. 4a and b are the IR spectra of the dried gel and the as-burnt powders in the range of 500–4000 cm^{-1}, respectively. The dried gel shows characteristic bands at about 1050, 1380, 1600, and 3300 cm^{-1}, which corresponds to the C—H bonding, NO_3^- ion, carboxyl group and O—H group respectively. The band at about 830 cm^{-1} also corresponds to the NO_3^- ion. The existence of the characteristic bands of NO_3^- indicates that the NO_3^- as a group exists in the structure of the dried gel.

As can be seen in Fig. 4b for the as-burnt powder, two characteristic bands arising from ionic carbonate (CO_3^{2-}) are shown in the spectrum near 840

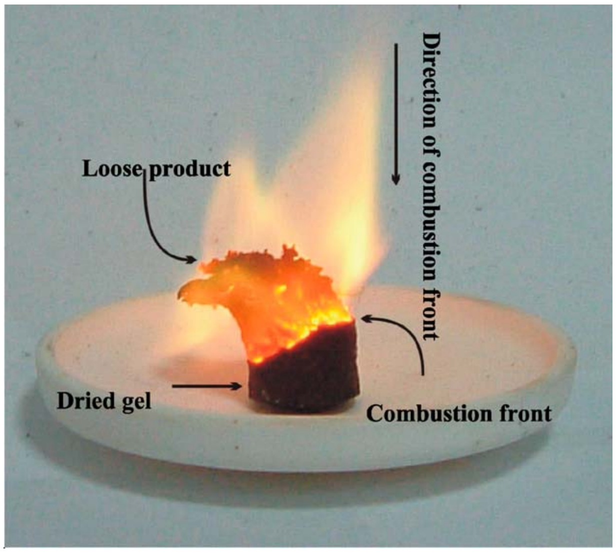

Figure 2 Self-propagating combustion of the dried gel.

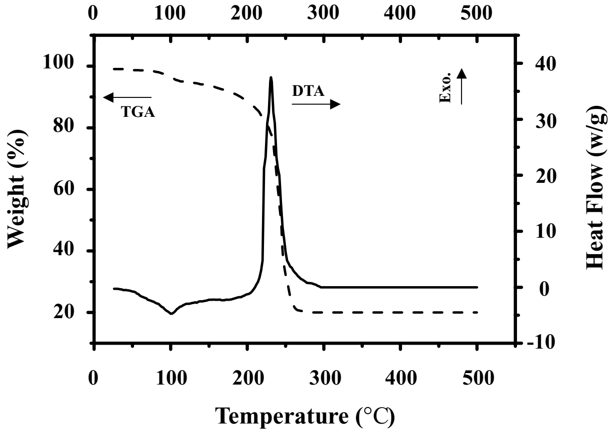

Figure 3 Typical TGA–DTA curves of the dried gel powder.

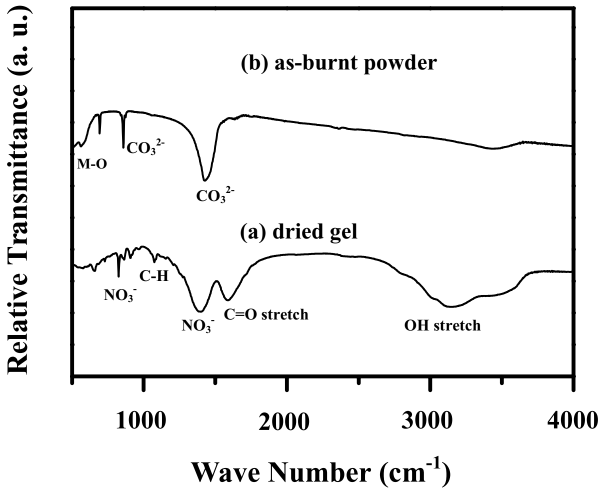

Figure 4 IR spectra of (a) the dried gel and (b) the as-burnt powder.

and 1450 cm^{-1}. In addition, a new peak appears at ~680 cm^{-1}, which is the bonding of metal and oxygen [17]. These peaks imply that the as-burnt powders may contain metal oxides and metal carbonates. This will be verified by XRD analysis (see below). The disappearance of the characteristic bands of C—H bonding, carboxyl group, and NO_3^- ion on the spectrum of the as-burnt powders reveals that the organic groups and NO_3^- ion take part in the reaction during combustion. Therefore, the combustion can be considered as a thermally induced anionic redox reaction of the dried gel wherein the citrate ion acts as a reductant and NO_3^- ion acts as an oxidant. Since NO_3^- ion provides an *in situ* oxidizing environment for the decomposition of the organic component, the rate of the oxidation reaction relatively increases, resulting in a self-propagating combustion of the dried gel.

Powder X-ray diffraction studies have been carried out on the dried gel, the as-burnt powder and the calcined powder, respectively. Fig. 5 shows the XRD patterns of the three samples. The dried gel powder is shown to be amorphous in nature. The characteristic peaks of Y_2O_3, $BaCO_3$, and CuO are detected in the XRD pattern of the as-burnt powder. This reveals that the dried gel converts to metal oxides after the combustion reactions. (It should be noted that BaO can absorb CO_2 easily from air and thus convert to $BaCO_3$ [18].) This is consistent with the result of IR spectrum analysis (see Fig. 4b). Moreover, the broadening of the XRD peaks indicates the as-burnt powder is submicron in size. The calcined powder is a single-phase Y123 with the orthorhombic perovskite-like structure, as shown in Fig. 5c. This indicates that the Y123 can be formed when the as-burnt powders were calcined at 900 °C for 12 hr.

Fig. 6a is a typical SEM photograph of the as-burnt powder. The powder is composed mostly of tiny particles (~0.1 μm), which are agglomerated, and there

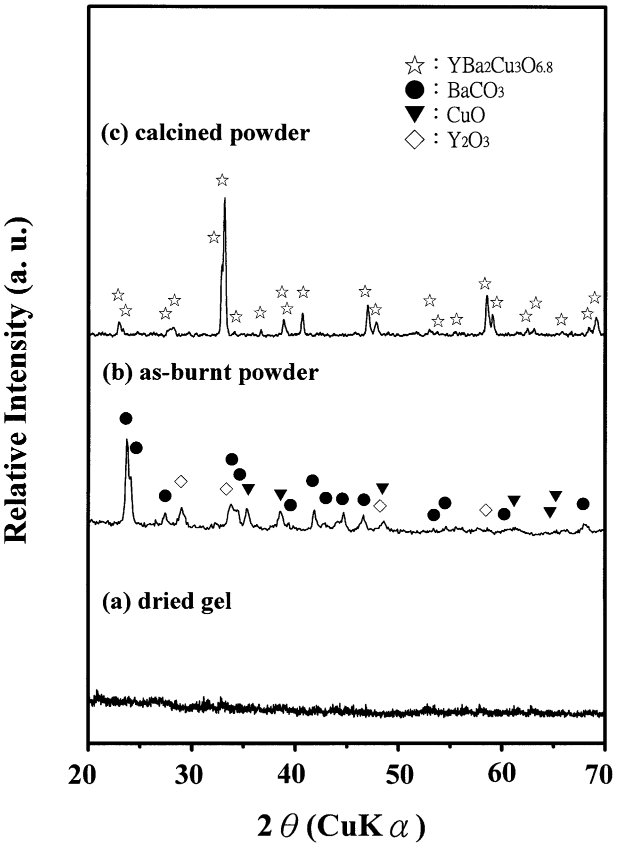

Figure 5 XRD patterns for (a) the dried gel, (b) the as-burnt powder, and (c) the calcined powder.

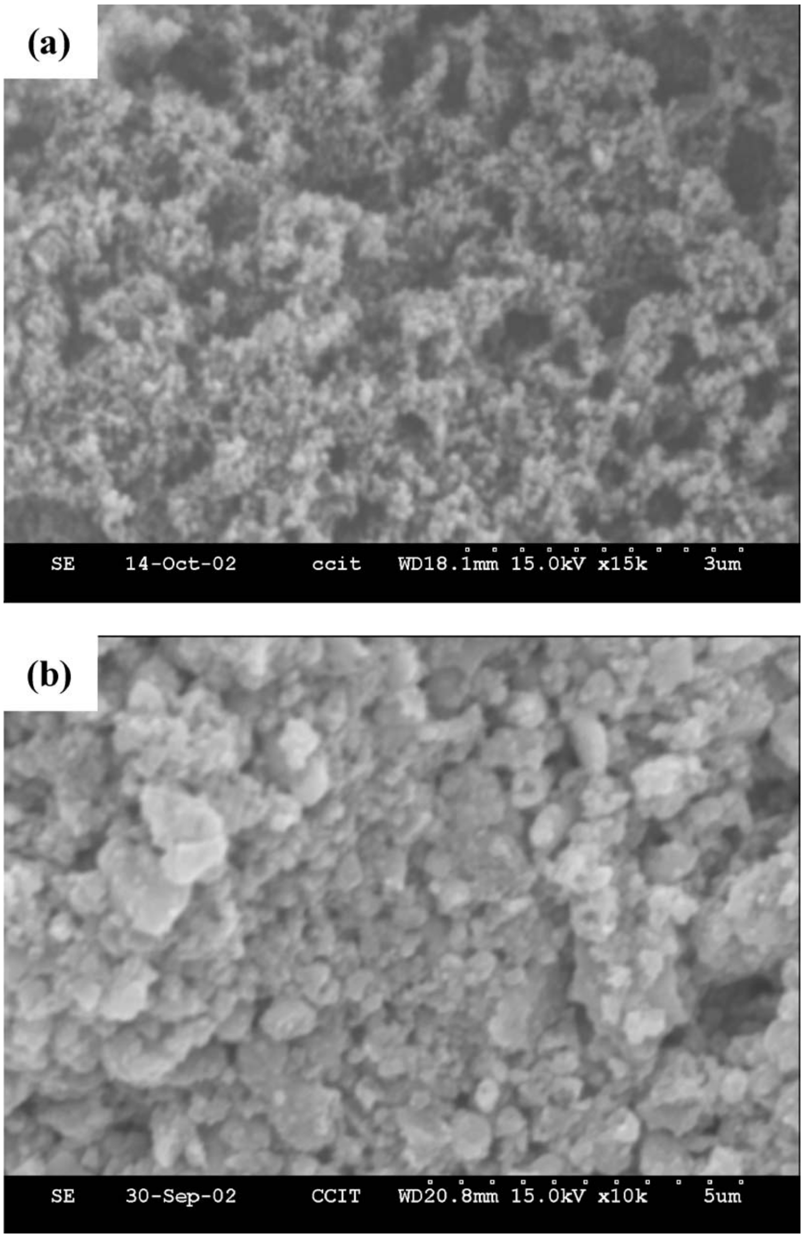

Figure 6 SEM photographs of (a) the as-burnt powder and (b) the calcined powder.

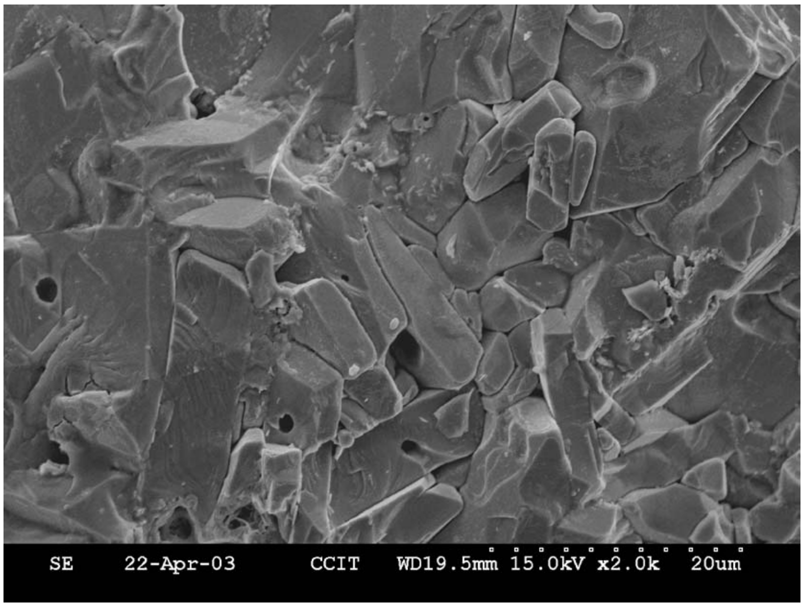

Figure 7 SEM photographs of the fracture surface of Y123 sintered at 930 °C for 6 hr.

is porosity throughout the sample. It is suggested that the as-burnt powders are loose and porous because of the evolution of a large amount of gases during the combustion reaction. Fig. 6b presents the general morphology of the calcined powder. The sample is composed mainly of agglomerated fine particles with diameters ranging from 0.2 and 1.5 μm. The specific surface area of the calcined powder is 10.83 m^2/g as obtained by Brunauer–Emmett–Teller (BET) analysis. Fig. 7 shows the SEM photograph for the fractured surface of the body sintered at 930 °C for 6 hr. A dense microstructure with a few pores can be observed from the photograph; moreover, the grains are more or less randomly oriented and elongated. The bulk density of the sintered body is 5.41 g/cm^2 ($\sim$90% of the theoretical value) determined by the displacement method using double-distilled water.

The variations of the magnetization and the electrical resistance versus temperature of the Y123 sample are shown in Fig. 8. As can be seen, the characteristic superconductive temperature determined by the magnetization measurement is consistent with that obtained from the resistance measurement, which appears to be 93 K. It was found that an Nd–Fe–B magnet could levitate above the sintered body immersed in liquid nitrogen (i.e., the Meissner effect). The sintered body is shown to possess the diamagnetic characteristic of high temperature superconductor by this phenomenon.

In conclusion, combining the sol–gel and combustion synthesis method, a novel way has been developed to prepare Y123 superconductors. The dried gel formed from metal nitrates and citric acid with the equal molar ratio exhibits a self-propagating combustion behavior once ignited in air at room temperature. The combustion process can be considered as an oxidation–reduction reaction, in which the NO_3^- ion is oxidant and citric acid is fuel. After combustion, the dried gel is transformed into a large amount of foamy ashes containing Y_2O_3, $BaCO_3$, and CuO. The as-burnt product requires to be calcinated at 900 °C for 12 hr, and then yields single-phase Y123 powder. Even so, this novel way is relatively simple, quick, efficient, and economical when compared with solid-state reaction methods and other wet-chemical routes.

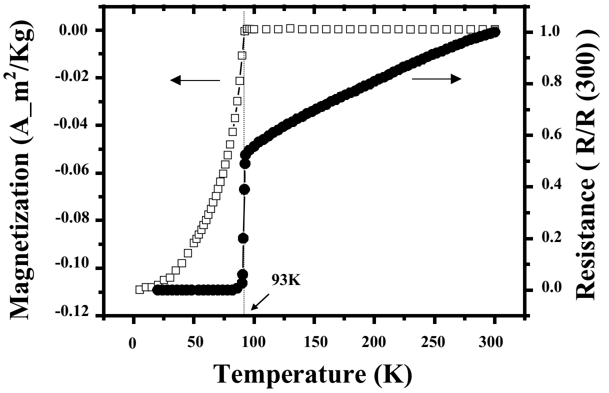

Figure 8 Temperature dependences of the normalized magnetization and resistance for Y123 sample prepared by the novel method.

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