Optimal Fuel Concentration and Heating Temperature for Solution Combustion Synthesis of $YBa_2Cu_3O_{7-x}$ High Temperature Superconductors

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***Abstract*— $YBa_2Cu_3O_{7-x}$ (Y123) ceramic superconductors have great potential for industrial applications. One of the challenges for utilizing Y123 in the applications is difficulty in synthesizing Y123 powders with desired composition. Solution combustion synthesis technique is known to be simple and cost-effective for synthesizing fine ceramic powders. This study aims at determining optimized conditions for Y123 powder synthesis. The powders were prepared by the combustion of aqueous solutions containing corresponding metal nitrate, acting as oxidizer, and sucrose, acting as combustion fuel. Fuel-to-oxidizer (f/o) ratios ranging from 1:3 to 3:1 and post-combustion heat treatment ranging from 850°C to 950°C were used in this experiment. Experimental results indicated that by varying f/o ratios and post-combustion heat treatment temperatures, compositions of the powders were altered. X-ray diffraction analysis revealed that Y123 powders with composition suitable for practical applications could be achieved in powders synthesized from all f/o ratio studied in this paper upon heating at 900°C for 4 hours. Formation of Y123 and other secondary phases with respect to f/o ratio and post-combustion heat treatment temperature will also be discussed.**

***Keywords*— Ceramics, Superconductors, $YBa_2Cu_3O_{7-x}$, Processing, Combustion Synthesis, Sucrose, Heat Treatment**

I. INTRODUCTION

High temperature superconductor materials have great potentials for industrial applications. The applications extend over a very wide range of industries, including electrical power industry--where superconductors are used as components of power cables, electrical motors and flywheel energy storage systems, transportation industry--where superconductors exploits their levitation capability in MagLev trains, and medical industry--where they are parts of Magnetic Resonance Imaging (MRI) systems, etc..

Among high temperature superconductors, the $YBa_2Cu_3O_{7-x}$ (Y123) system receives the most attention due to the following reasons: (i) it is one of the first high temperature superconductors to be discovered; (ii) it has much simpler structure compared to some other higher temperature superconductors; (iii) it has very sharp superconducting transition temperature (T_c); (iv) Y123 consists of elements which are not extremely toxic; (v) Y123 crystals are easily fabricated; and (vi) magnetic and electrical properties of Y123 can be easily manipulated by tailoring the internal defects of the system.

One of the challenges for utilizing Y123 superconductors in the applications is difficulty in synthesizing Y123 powders with desired composition. Uncontrolled synthesis process of Y123 often causes formation of non-superconducting phase, such as $Y_2Ba_4O_7$, $BaCuO_2$, $Y_2Ba_2O_5$ and Y_2BaCuO_5 (Y211) [1-2]. The presence of non-superconducting phases may contribute to alteration of physical characteristics, as well as reduction of superconducting properties of the powders. Therefore, it is crucial that the synthesis process of Y123 powder needs to be well-monitored.

Solution combustion synthesis technique is known to be a simple and cost effective process for synthesizing ceramics powders. The solution combustion synthesis process involves a self-sustained reaction in solution of metal nitrate, acting as oxidizers, and organic matters such as urea, glycine, hexamethylenetetramine, dextrose and sucrose, acting as fuel [3-5]. In addition to simplicity and cost effectiveness, the solution combustion synthesis process can also be used to produce very fine ceramics powders with desired composition. Studies from many research groups revealed that the solution combustion synthesis process were employed for production of homogeneous, nano-sized ceramics powder [6-7].

It has been reported that the organic fuel used in the solution combustion process plays a significant role in controlling the composition of powder product [8]. However, effects of fuel concentration and post-combustion heat treatment on powder compositions have not been clearly examined. This study is, therefore, aimed at investigating the

effect of the fuel concentration and the post-combustion heat treatment on the composition of the Y123 powder prepared by the solution combustion technique. Fuel-to-oxidizer (f/o) ratios ranging from 1:3 to 3:1 and post-combustion heat treatment with temperature ranging from 850°C to 950°C were employed in this experiment. X-ray diffraction technique was utilized in identifying composition of the powder product.

II. Experimental Procedure

The powders were synthesized by solution combustion synthesis process, which involved mixing of aqueous solutions containing metal nitrate and combustion fuel together prior to heating. The metal nitrate solution was prepared by dissolving $Y(NO_3)_3{\cdot}6H_2O$, $Ba(NO_3)_2$ and $Cu(NO_3)_2{\cdot}3H_2O$ (Aldrich) with stoichiometric ratios of Y:Ba:Cu = 1:2:3 in distilled water. Sucrose, the fuel employed in the present study, was then added to the prepared nitrate solution. The fuel-to-metal ion molar ratio**,** commonly known as fuel-to-oxidizer (f/o) ratios**,** was varied from fuel-deficient (f/o = 1:3), exact stoichiometry (f/o = 1:1), to fuel-rich conditions (f/o = 3:1).

The clear, bluish solution containing metal nitrates and fuel was placed on a hot plate capable of heating at 380°C. The solution then boiled and ignited with a flame. Upon completion of combustion reaction, the products were collected and ground into powders with a mortar and pestle. Subsequently, the powders were heated with temperature ranging from 850°C to 950°C for 4 hours.

Composition of the powders were investigated by X-ray diffractometer (Phillips X'Pert), over angles ranging from 20° to 60° in 2θ, with a step size of 0.01° and a scan rate of 1.3 °/min.

III. Results and Discussion

A. Color Characteristics of Powders

A total of 12 powder products synthesized at various conditions were obtained. Colors of the synthesized powder can provide some information related to composition of the powders. It has been recognized that that the $YBa_2Cu_3O_{7-x}$ (Y123) superconductor powder is black in color, while the Y_2BaCuO_5 (Y211) non-superconducting phase is green.

For the powders prepared under fuel-deficient condition (f/o = 1:3), the colors of powder varied upon heating temperature. Without post-combustion heating, powder was grayish in color, suggesting that the powder may not be pure Y123. It was observed that powders subjected to post-combustion heating at 850 and 900°C turned black, suggesting that the powder may consist of Y123. However, at high heating temperature of 950°C, the color of the powder was black with greenish mixture. The results implied that the powder may consist of Y123 and Y211 phase.

For the powders prepared under exact stoichiometry and fuel-rich condition (f/o = 1:1 and 3:1), a color transformation similar to fuel-deficient powders was observed in powders without heating and heated at 850 and 900°C. The un-heated powders were dark gray, while powders subjected to heating at 850 and 900°C were black. At the highest heating temperature of 950°C, the powders prepared under exact stoichiometry and fuel-rich condition was dark green, suggesting that the powders may primarily consist of Y211 non-superconducting phase.

Color observation generally suggested that without post combustion heat treatment, powders may not contain Y123. At post combustion heating of 850 and 900°C, the powders may transform to Y123 phase, while turning to Y211 phase when heating at 950°C. However, these observations may not provide precise identification of powder compositions. Accurate phase identification was conducted by x-ray diffraction analysis, which would be discussed in the next section.

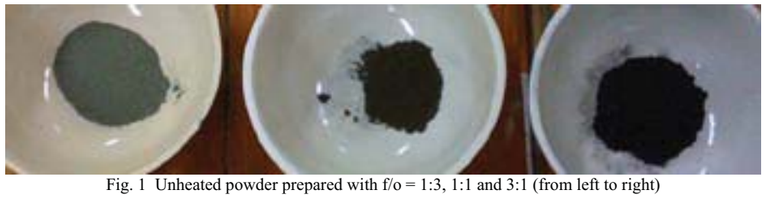

Fig. 1 Unheated powder prepared with f/o = 1:3, 1:1 and 3:1 (from left to right)

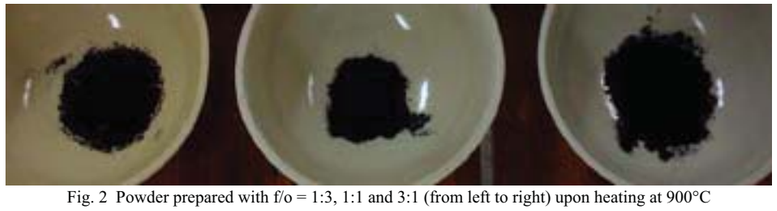

Fig. 2 Powder prepared with f/o = 1:3, 1:1 and 3:1 (from left to right) upon heating at 900°C

Fig. 3 Powder prepared with f/o = 1:3, 1:1 and 3:1 (from left to right) upon heating at 950°C

B. Compositions of Powders

Compositions of synthesized powder were identified by x-ray diffraction analysis. The analysis was conducted by matching the 2θ positions of prominent peaks from diffraction results with the patterns obtained from JCPDS database. The x-ray analysis showed that various compounds, primarily Y123 (JCPDS # 76-0657), Y211 (JCPDS # 80-0770), $BaCO_3$ (JCPDS # 71-2394), $Ba(NO_3)_2$ (JCPDS # 76-0920), were evident in the powder products.

The x-ray results, as shown in table 1 and Figs 4-6, revealed that the post-combustion heat treatment temperatures had a significant effect on powder composition. For powders prepared under fuel-deficient conditions (f/o = 1:3), the x-ray analysis showed that the unheated powder primarily consisted of $Ba(NO_3)_2$, which was the initial reagent used in the combustion. The color of $Ba(NO_3)_2$ is white. When combined with blackish powder of Y123 or other Ba-Cu rich phases, the powder turned gray. The x-ray results corresponded well with results from the previous section.

The results indicated that combustion reaction was not completed at a severe fuel-deficient condition. However, as the powders were heated at 850 and 900°C, formation of Y123 occurred. The result suggested that heat treatment was required for formation of Y123 under fuel-deficient condition. For powder heated at 950°C, the x-ray analysis revealed that the primary phase was Y123 and Y211. By considering chemical formula of Y123 and Y211, it was apparent that $YBa_2Cu_3O_{7-x}$ (Y123) had a higher Cu concentration than Y_2BaCuO_5 (Y211). Therefore, it was possible that at higher fuel concentration, higher temperature combustion occurred, leading to decomposition of Cu. As a result of Cu deficiency, formation of Y211 occurred.

For powders prepared under exact stoichiometry (f/o = 1:1), the un-heated powder primarily consisted of $BaCO_3$. Formation of $BaCO_3$ was believed to be attributed to a reaction between Ba^{2+} ions from $Ba(NO_3)_2$ and carbon from sucrose. Phase transformation similar to fuel-deficient powders was observed upon heating. Upon heating at 850 and 900°C, the powders were identified as Y123.

Phase identification was also conducted in powders prepared under fuel-rich condition (f/o = 3:1). Powders without heat treatment mainly consisted of $BaCO_3$, while Y123 was the primary phase of powders subjected to heating at 850 and 900°C. In addition to Y123, $BaCO_3$ was also observed in the powder heated at 850°C. The result suggested that excess sucrose could lead to formation of a significant quantity of $BaCO_3$. The remaining $BaCO_3$ in the powder after heated at 850°C seemed to support the observation. At post combustion heating of 950°C, the powder primarily consisted of Y211. Formation of Y211 might be attributed to the decomposition of Cu, as explained previously.

TABLE I
Summary of primary phases observed in powder prepared under various conditions

Heating Conditions	**Fuel-to-oxidizer (f/o) Ratios**		
	1:3	**1:1**	**3:1**
No post-combustion heating	$Ba(NO_3)_2$	$BaCO_3$	$BaCO_3$
Heated @ 850°C	Y123	Y123	Y123 / $BaCO_3$
Heated @ 900°C	Y123	Y123	Y123
Heated @ 950°C	Y123/Y211	Y123 / Y211	Y211

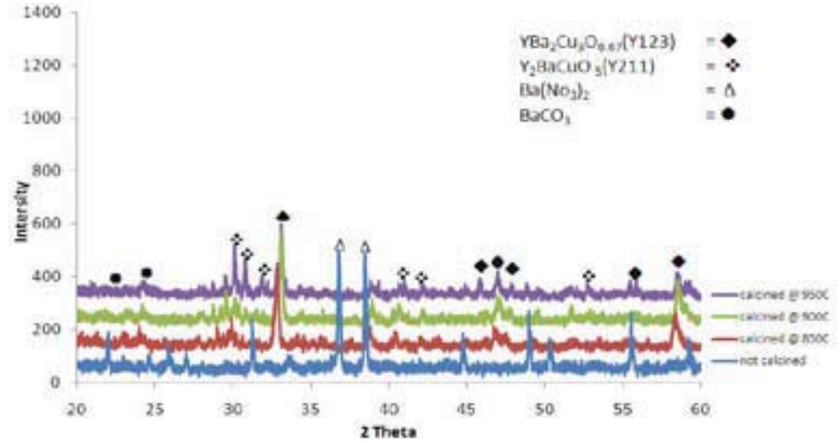

Fig. 4 X-ray diffraction pattern of powders prepared under fuel-deficient condition

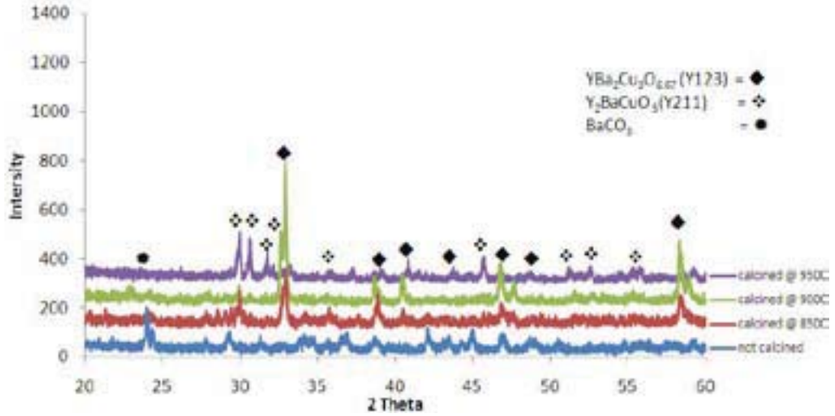

Fig. 5 X-ray diffraction pattern of powders prepared under exact stoichiometry

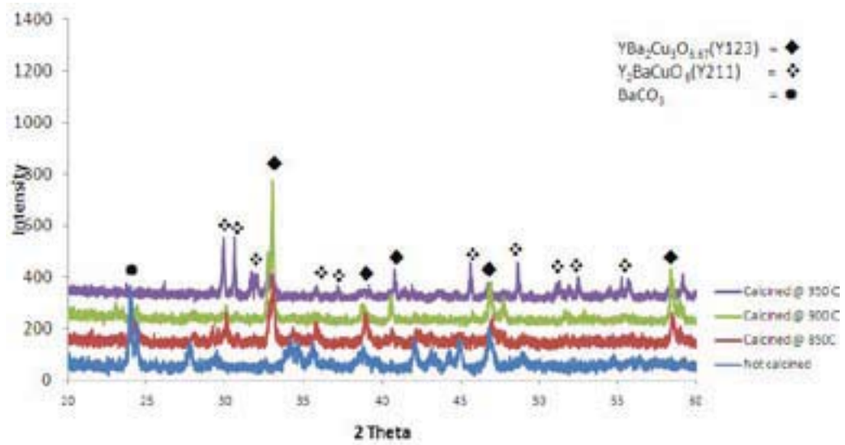

Fig. 6 X-ray diffraction pattern of powders prepared under fuel-rich condition

TNI Journal of Engineering and Technology
Vol.2 No.1 January - June 2014

IV. Conclusions

Effects of fuel concentration and post-combustion heating temperatures on compositions of powders synthesized by solution combustion synthesis were investigated in this study. Color characteristic of synthesized power corresponded well to the x-ray diffraction results, which indicated that by varying fuel-to-oxidizer (f/o) ratios and post-combustion heat treatment temperatures, compositions of the synthesized powders were altered.

Under fuel-deficient conditions (f/o = 1:3), incomplete combustion reaction occurred, which resulted in the remaining initial oxidizer, $Ba(NO_3)_2$. At higher fuel concentrations, excess carbon from fuel led to formation of a non-superconducting phase, $BaCO_3$. The post-combustion heat treatment had a significant effect on transformation of these undesired non-superconducting phases into Y123 powders. At heating temperature of 900°C, powders prepared under all f/o ratio (1:3, 1:1 and 3:1) transformed into the Y123 superconducting phase. However, while heating at 950°C, formation of Y211 non-superconducting phase occurred. This may be attributed to the decomposition of Cu at high temperature.

The results revealed that the optimal condition for synthesizing Y123 superconductor powder was the post combustion heat treatment at 900°C, regardless of the fuel concentration. In another word, to obtain the Y123 superconductor suitable for practical applications, the powder could be synthesized by the combustion technique with subsequent heat treatment at 900°C.

This study, however, did not include the information related to examination of superconducting properties of the powder. Hence, further investigation regarding electrical or magnetic properties of the Y123 superconductor power is required as the next step of the study.

Acknowledgment

Financial and equipment support from Thailand Research Fund and Department of Materials Engineering, Kasetsart University are gratefully acknowledged. Authors also wish to acknowledge Mr. Payoon Saenthongkaew for assistance in x-ray diffraction analysis.

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