EFFECT OF THE CALCINATION TEMPERATURES ON $YBa_2Cu_3O_{7-X}$ POWDER STOICHIOMETRY

Poom Prayoonphokkharat,[1] Sukanda Jiansirisomboon,[1,2] Anucha Watcharapasorn[1,2,*]
[1] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[2] Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
*e-mail: anucha@stanfordalumni.org

Abstract: This research, the influence of calcination temperature on $YBa_2Cu_3O_{7-x}$ (YBCO) powder stoichiometry was studied. The YBCO powder was synthesized by solid-state reaction of mixed Y_2O_3, $BaCO_3$ and CuO powders. The mixed powder was calcined in air at 800 – 950 ^oC for 12 h. X-ray diffraction (XRD) analysis showed that phase-pure YBCO could be produced using calcination temperature in the range 850 – 900 ^oC. Microstructural and compositional studies using a scanning electron microscope (SEM-EDX) also showed the powder size of about 1-2 μm with very near in tended stoichiometry. All other calcination temperatures used in this study showed a presence of impurity phases either due to incomplete reaction or material loss. The change in calcination temperature was also found to affect the stoichiometric ratio in single-phase YBCO compound.

Introduction: $YBa_2Cu_3O_{7-x}$ (YBCO) is one of the most early founded and interesting high-T_c superconductor. The material is known to possess high irreversibility field (H_{irr}) and high current density (J_c). Therefore, its intended use has been in electronic applications such as magnet, chemically active sensor, low-loss transformer and generator.[1-2] The previously reported synthesis methods included solid-state reaction of oxalates or carbonates, coprecipitation[3], thermal decomposition of heteronuclear complex[4] and spontaneous reaction synthesis (SRS).[5] Some methods could produce high-quality powder but the small quantity of resulting powder and complicated process often restricted their commercial use. The solid-state reaction route is thought to be a promising, it is a simple process and can produce high quantity of good-quality powders.

YBCO is an oxygen-deficient compound with triple perovskite unit cell in which Y and Ba reside at A-site and B-site cations, respectively. It is well known that YBCO is highly oxidizing and tends to lose oxygen during synthesis process at high calcination temperature.[6] The missing oxygen has been a major factor causing the stoichiometric change in YBCO. Generally, the oxygen content in YBCO can vary over the range $0 < x < 1$ with electrical transition from superconducting state ($x < 0.5$) to semiconducting behavior ($x > 0.5$) and corresponding crystal-structure change from orthorhombic to tetragonal.[2] Furthermore, the superconducting critical temperature (T_c) is also dependent on oxygen content and found to decrease from approximately at ~90 K (for $x < 0.5$) to ~60K (for $x > 0.5$). The typical processing conditions of superconducting YBCO therefore involved synthesis under oxygen flow atmosphere for preventing oxygen loss. Despite provided excess oxygen, some synthesis results still showed non-stoichiometric powder and secondary phases such as $BaCuO_2$ (001 phase) and Y_2BaCuO_5 (211 phase).[3]

In this research, we study the influence of calcination temperature on YBCO powder stoichiometry by solid-state reaction method using mixed oxide and carbonate starting compounds under normal air atmosphere. The relationship between calcination temperature, phase and composition were investigated and discussed.

Methodology: The $YBa_2Cu_3O_{7-x}$ powders were prepared by conventional solid-state reaction method by using a stoichiometric amount of Y_2O_3 (99.99 %, Aldrich), $BaCO_3$

(≥ 99 %, Sigma-aldrich) and CuO (98%, Sigma-aldrich). The raw materials were mixed with ethanol and milled in a polyethylene jar with zirconia ball for 24 h. The mixed powders were dried, regrounded and calcined in an alumina crucible. The calcination temperatures of powder ranged from 800 to 950 ^{o}C and 12 h under normal air atmosphere. The calcined powders were reground and sieved for homogeneous distribution.

The powders were characterized for phase formation by X-ray diffraction (XRD) using X-ray diffractometer (Rikagu Miniflex II) with Cu Kα (λ = 1.5405 Å). The step size of diffraction (2θ) were 0.015^{o} and X-ray patterns were collected in the range of 2θ = 20 to 80^{o} at a scanning rate of 5^{o}/min. The powder morphologies were investigated using a scanning electron microscope (JEOL – JSM5910LV) operated at 15 kV. The chemical composition identification for stoichiometry analysis was analyzed using energy dispersive X-Ray analysis (SEM-EDX).

Results and Discussion: The XRD patterns of YBCO powder synthesized at different calcination temperatures shown in Figure 1. It could be seen that the main peaks corresponded to the standard pattern of YBCO-123 (JCPDS File No. 39-0486).[7-8] The crystal structure of powders prepared were orthorhombic perovskite. At the calcination temperature of 800 ^{o}C, $BaCO_3$ phase ~14% was observed. In this case, the calcination temperature was not enough for complete decomposition of the carbonate, so this was the rate-limiting step for reaction. In addition, other observed impurity phases such as Y_2CuO_5 and CuO (each about 2%) were also mentioned in other reports.[3,6,9] When the calcination temperature increased to 850 ^{o}C and 900 ^{o}C, pure YBCO-123 phase was obtained. The minor differences of their XRD patterns such as those of (013)/(103) and (123)/(213) peaks were due to compositional variation in powder as well as crystallite size. Furthermore, the intensity of peaks (012), (112) and (115) of the sample calcined at 900 ^{o}C was lower than that of 850 ^{o}C. This could be due to the preferred orientation effect of crystallites. At maximum calcination temperature of 950 ^{o}C, the intensity of 00*l* peaks was found to increase from preferred orientation effect. Moreover, about 2% of unknown phase was present which could be due to the fact that the temperature was too high which resulted in material loss.[10]

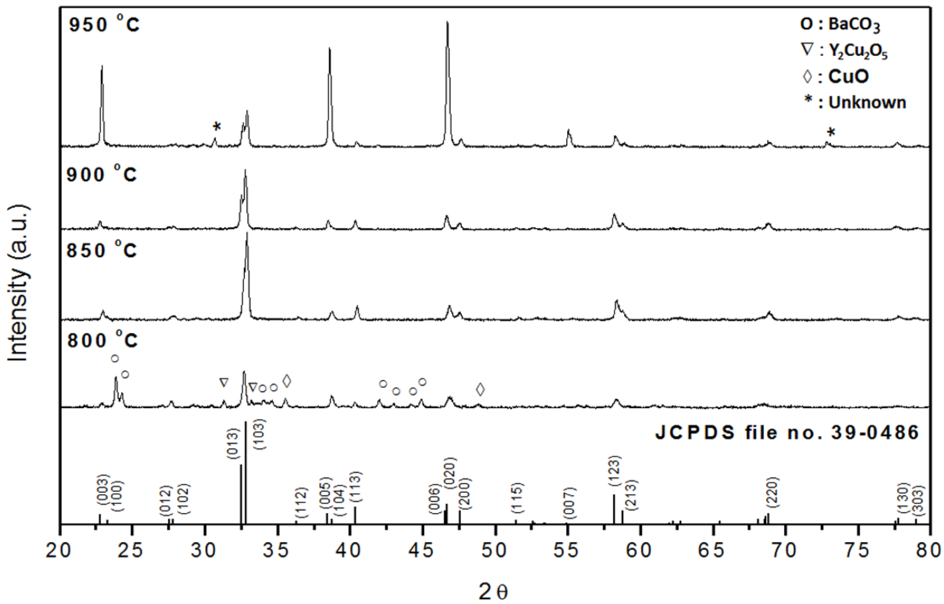

Figure 1. XRD patterns of YBCO calcined at 800 – 950 ^{o}C for 12 h

The results of microstructural investigation of YBCO powders are shown in Figure 2. It was found that, for 800 ^oC, the particles of powder consisted of two main types. The first type was YBCO-123 particles having grain-size distribution of < 1 μm and the second was those having particle size in a range of 1.5 – 3 μm. EDX analysis of the latter showed Ba-Cu-O elements, which were in agreement with $BaCO_3$ and CuO found in XRD pattern. When the calcination temperature was increased to 850 ^oC, the particle size increased with somewhat narrower size distribution. A further increase in calcination temperature to 900 ^oC and 950 ^oC caused the average grain size to increase to 1-2 μm and > 2 μm, respectively. These large grains came from the agglomeration of particles and the growth of primary particle when the calcination temperature was increased.[3]

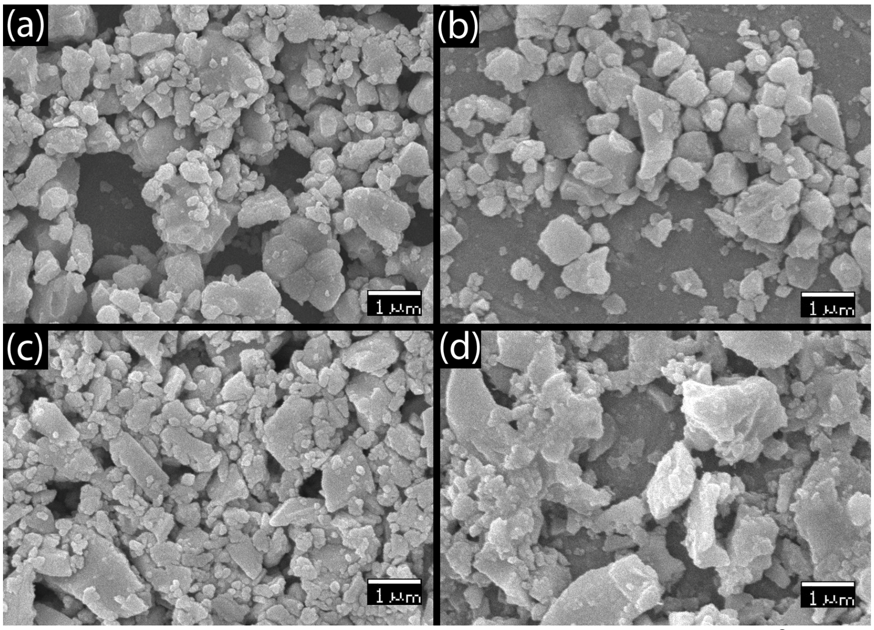

Figure 2. SEM micrographs of YBCO powder calcined at (a) 800 ^oC (b) 850 ^oC (c) 900 ^oC and (d) 950 ^oC for 12 h.

The elemental and stoichiometry analysis by EDX of pure YBCO powder (850 ^oC and 900 ^oC) is shown in Table 1. It was found that the stoichiometry of YBCO-123 powders varied with calcination temperature. At 850 ^oC, the elemental ratios of Ba/Y ~ 2.14, Cu/Y ~ 3.18 and O/Y ~ 6.59, resulting in a nominal composition $YBa_{2.14}Cu_{3.18}O_{6.59}$. Compared to the stoichiometric ratio of YBCO-123, the deviation was in a range of 1.90 – 3.94 %. For sample calcined at 900 ^oC, the amount of oxygen was reduced to 34.29 at.% because of its loss during firing when reaction was proceeding.[5,9] In case of 800 and 950 ^oC, stoichiometry of YBCO phase was affected by the presence of impurity phases and, hence, direct effect of temperature on YBCO composition therefore could not be deduced.

Table 1. EDX result for nominal composition of pure YBCO with different calcination temperatures

Calcination Temperature (^oC)	Element Composition (at.%)				Composition Error (%)			
	Y	Ba	Cu	O	Y	Ba	Cu	O
$YBa_2Cu_3O_{6.5}$	8	16	24	52	-	-	-	-
850	7.74	16.63	24.62	51.01	3.25	3.94	2.58	1.90
900	10.62	21.66	33.43	34.29	32.75	35.38	39.29	34.06

Conclusion: This experiment showed the influence of calcination temperatures on solid-state synthesis of $YBa_2Cu_3O_{7-x}$ powders using Y_2O_3, $BaCO_3$ and CuO as raw materials. X-ray analysis indicated pure phase of YBCO when calcined at 850 – 900 ^{o}C. For lower and higher temperatures, raw materials partially remained and second phase was present, respectively. The stoichiometric ratio of pure YBCO powder also changed with calcination temperature. Compared to the stoichiometry of standard YBCO-123, the optimum synthesis condition was found to be 850 ^{o}C and 12 h dwell time.

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