

COMPOSITION AND PARTICLE SIZE OF $\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ SUPERCONDUCTOR POWDERS SYNTHESIZED BY SOLID STATE REACTIONS

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Abstract

$\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ (RE: Y and Sm) superconductors have great potential for industrial applications. However, exploitation of the RE123 materials is often hindered by impurities in the RE123 powder. This project aims at studying the composition and particle size of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Y123) and $\text{SmBa}_2\text{Cu}_3\text{O}_{7-x}$ (Sm123) powders synthesized using the solid state reaction technique. Initial reagents, consisting of nitrates of rare-earth elements, $\text{Ba}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, were mixed and calcined at 900°C . X-ray diffraction (XRD) analysis of the calcined powders showed the desired chemical compositions, which contain $\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ (RE123) and $\text{RE}_2\text{BaCuO}_5$ (RE211). However, a small amount of impurities such as BaCO_3 and BaCuO_2 remained. The XRD results agreed with the differential thermal analysis results, which indicated that decomposition of BaCO_3 occurs at temperatures higher than 900°C . Scanning electron micrographs revealed that the particles had irregular shapes and were clustered into agglomerates. Average particle sizes were $4.67\ \mu\text{m}$ and $3.54\ \mu\text{m}$ in the Y123 and Sm123 powders, respectively. A wide distribution of these particle sizes was also observed.

Keywords: Superconductor, RE123, solid state reaction, powder synthesis

Introduction

$\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ (where RE is a rare-earth element) high temperature superconductors attract extensive attention from researchers due to their potential for various practical applications. These include superconducting magnetic energy storage systems, high-temperature superconducting quantum interference devices, thin film superconductor electromagnetic radiation detectors, high-temperature superconductor power cables, superconducting

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microchips, and superconducting magnets used by Maglev trains.

The problems related to chemical inhomogeneity and impurities of the superconducting powders, however, hinder the potential utilization of superconductors in practical applications. Powder synthesis has a large influence on chemical homogeneity, purity, and the final properties of ceramic materials. It has been reported that the formation of non-superconducting phases such as BaCO_3 , which often occurs in the uncontrolled synthesis processing of RE123, leads to the suppression of critical current density in superconductors (Goretta *et al.*, 1988; Balachandran *et al.*, 1989). Synthesis of superconducting powders is, therefore, one of the most important steps in the field of superconductor processing.

Various powder processing techniques can be employed in synthesizing superconducting powders. Some of the most conventional techniques are comprised of co-precipitation, sol-gel, combustion synthesis, and solid-state reactions. Relatively homogeneous RE123 powders with a small particle size can be attained by the co-precipitation technique. However, to achieve complete co-precipitation, and to obtain phase-pure powders, the synthesis process must be well controlled. The powders with the desired composition can be synthesized only under precise pH and temperature conditions (Pathak and Mishra, 2005). In addition, inhomogeneity of powders produced by the co-precipitation method can appear if uneven distribution of the pH value occurs. For some precipitation systems employing potassium hydroxide to control the pH value, contamination of potassium ions may also occur. This leads to undesirable stoichiometry (Chang and Liu, 1990).

The sol-gel technique also produces homogenous powders. However, to attain powders which have the desired composition using the sol-gel technique, processing parameters such as starting precursors, the solvent, the pH of the sol, and the calcination temperature must be carefully controlled (Ravindranathan *et al.*, 1988). Additionally,

the sol-gel technique generally involves high-cost raw materials and potentially health-hazardous organic solutions. Residual hydroxyl and carbon remaining in the samples may be other disadvantages of the sol-gel technique (Brinker and Scherer, 1990).

The solution combustion synthesis process is a simple and rapid process that involves a self-sustained reaction in a solution of metal nitrate and organic fuels. In addition to simplicity and cost effectiveness, the solution combustion synthesis process can produce very fine ceramic powders with the desired composition. Studies from many research groups reveal that the solution combustion synthesis process has been successfully employed for the production of homogeneous, nano-sized ceramic powders (Mimani and Patil, 2001; Singanahally and Mukasyan, 2008). However, incomplete combustion reactions may occur, resulting in residual initial chemical reagents. A calcination process is subsequently required for elimination of these undesired initial phases (Jongprateep and Tanmee, 2012).

The solid state reaction is a conventional ceramic process known to be simple and cost effective for synthesizing ceramics powders. In addition, this technique produces powder with a high yield. However, production of phase-pure powder with a small particle size using solid state reactions remains challenging. Non-superconducting phases, specifically initial chemical reagents and BaCO_3 which are linked to suppression of superconducting properties in RE123, are often observed in the RE123 powder synthesized by the solid state reaction technique. In order to minimize the formation of the non-superconducting phases, the thermal evolution of the reaction needs to be examined. This study, therefore, examines the composition and particle size of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Y123) and $\text{SmBa}_2\text{Cu}_3\text{O}_{7-x}$ (Sm123) powders synthesized by the solid-state reaction technique along with the thermal evolution of the synthesized powders during heat treatment.

Materials and Methods

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Y123) and $\text{SmBa}_2\text{Cu}_3\text{O}_{7-x}$ (Sm123) powders were prepared using the solid state reaction technique. To obtain compositions of Y123 and Sm123, metal nitrate reagents, specifically $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (RE: Y and Sm), $\text{Ba}(\text{NO}_3)_2$, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ powders (Aldrich), were mixed and round in a mortar with a mole ratio of $\text{RE}^{3+} : \text{Ba}^{2+} : \text{Cu}^{2+} = 1:2:3$. The powder mixtures were subjected to calcination at 900°C for 6 h with a heating and cooling rate of $10^\circ\text{C}/\text{min}$. The calcination process was repeated over 2 cycles with intermediate grinding.

X-ray diffraction (XRD) of the calcined powders was examined for phase identification. A Phillips X'Pert x-ray diffractometer (Koninklijke Philips Electronics N.V., Amsterdam, Netherlands) with $\text{CuK}\alpha$ radiation was employed in the XRD analysis. Measurements were conducted over angles ranging from 20° to 60° in 2θ , with a step size of 0.01° , and a scan rate of $1.3^\circ/\text{min}$. Thermal analysis of the powders was conducted on uncalcined powder mixtures under a flowing air atmosphere using a Perkin Elmer DTA7 (PerkinElmer, Inc, Waltham, MA, USA), with the temperature ranging from room temperature to 1100°C . Decomposition temperatures of the powders were determined at the onset of the

differential thermal analysis (DTA) curves. Particle sizes of the synthesized powders were estimated microscopically using a scanning electron microscope (Phillips XL30, Koninklijke Philips Electronics N.V., Amsterdam, Netherlands). The size distribution of the particles was analyzed using Scion Image Software (Informer Technologies, Inc., Roseau Valley, Dominica). A minimum of 100 particles was counted to obtain the average size of the particles.

Results and Discussion

Powder Composition

The composition of the synthesized powders was identified using XRD. The XRD analysis was conducted by matching the 2θ positions of prominent peaks from the diffraction results with the patterns obtained from the Joint Committee on Powder Diffraction Standards' database. Figure 1 shows the diffraction patterns of Y-Ba-Cu-O powders subjected to 1 and 2 calcination cycles, while Sm-Ba-Cu-O powders subjected to 1 and 2 calcination cycles are presented in Figure 2. Results from the XRD indicate that the major peaks correspond to $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Y123) and $\text{SmBa}_2\text{Cu}_3\text{O}_{7-x}$ (Sm123). The primary phases of Y123 and Sm123 were

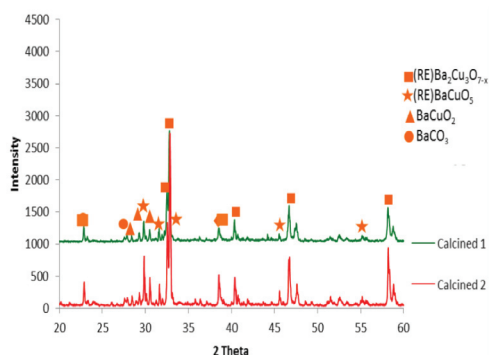


Figure 1. X-ray diffraction patterns of Sm-Ba-Cu-O powders subjected to 1 and 2 calcination cycles

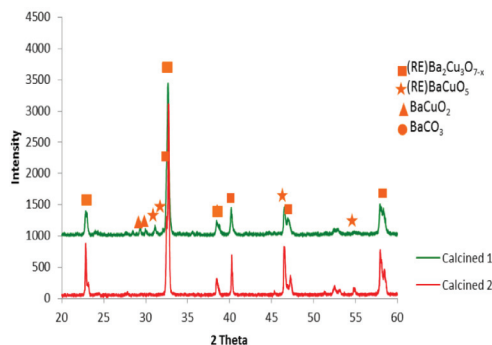


Figure 2. X-ray diffraction patterns of Y-Ba-Cu-O powders subjected to 1 and 2 calcination cycles

represented by the peaks $2\theta = 23, 33, 38, 40, 47, \text{ and } 58$. The patterns exhibited only small peaks representing BaCO_3 and $\text{Ba}(\text{NO}_3)_2$ which were mostly eliminated after the second calcination. The XRD pattern also exhibited the phases commonly present along with RE123, identified as $\text{RE}_2\text{BaCuO}_5$ (RE211) and BaCuO_2 .

As mentioned previously, the presence of BaCO_3 could have a detrimental effect on the superconductivity of RE123. Different from the BaCO_3 phase, RE211 and BaCuO_2 do not play a significant role in suppressing the critical current density of the superconductors. On the contrary, the presence of the RE211 phase is beneficial to its superconducting properties.

One of the imperative requirements for utilizing RE123 superconductors in practical applications is the high critical current density. Improvements to the critical current density of superconductors can be achieved through the enhancement of flux pinning. The interface between the superconducting matrix and second-phase particles can play a significant role in flux pinning enhancement (Jongprateep *et al.*, 2005). Incorporation of RE211 particles into the RE123 superconducting phase has been proven experimentally to be favorable for a high critical current density. It was reported that interfaces between RE211 particles and the RE123 matrix could play a role as flux pinning centers. In addition to critical density enhancement, the presence of

the RE211 phase can reduce the residual liquid phase, and diminish the formation of porosity and microcracks (Heuberger *et al.*, 1987).

Experimentation results from the current study indicates that an impurity phase that had detrimental effects on the superconducting properties was eliminated, while the beneficial phase still remains after the second calcination process is completed. The results, therefore, suggest that 2 calcination cycles should be completed in order to create superconducting powders with compositions suitable for practical applications.

Thermal Evolution

Differential thermal analysis DTA of the Y-Ba-Cu-O and Sm-Ba-Cu-O powders is presented in Figure 3. Thermal analysis of the powder mixture indicates the decomposition of $\text{Ba}(\text{NO}_3)_2$, represented by endothermic peaks around 800°C . The observation of strong endothermic peaks around 920°C is due to the decomposition of BaCO_3 . Results from the DTA correspond well with the x-ray analysis, which demonstrates that the $\text{Ba}(\text{NO}_3)_2$ and BaCO_3 peaks were mostly eliminated after calcination at 900°C . Strong endothermic peaks were evident in the Y-Ba-Cu-O and Sm-Ba-Cu-O powders around 960°C and 1020°C , respectively. These endothermic reactions represent peritectic decomposition of Y123 and Sm123. The results suggest that, in order to completely eliminate undesirable phases such as BaCO_3 , a slight increase of the calcination temperature might be required.

Powder Morphology and Particle Size

The morphology and particle size of the powders produced by the solid state reaction technique were determined by a scanning electron microscope (SEM). SEM micrographs revealed irregularly shaped particles, which were linked together in agglomerates of different sizes, as shown in Figures 4 and 5.

Differences in the average particle sizes between the powders subjected to 1 and 2 calcination cycles were not significant. The average particle sizes of the Y123 powders

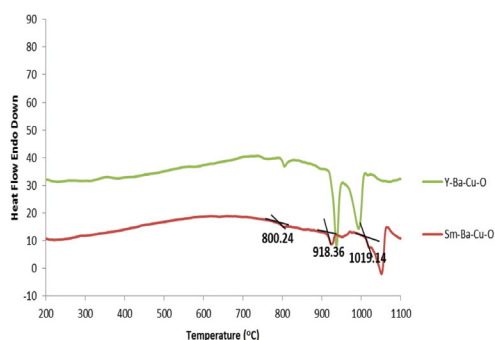
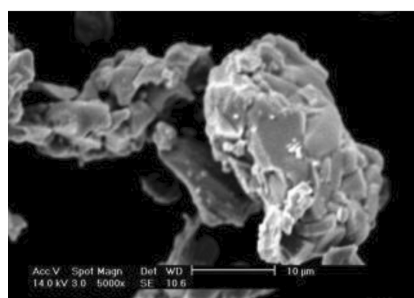


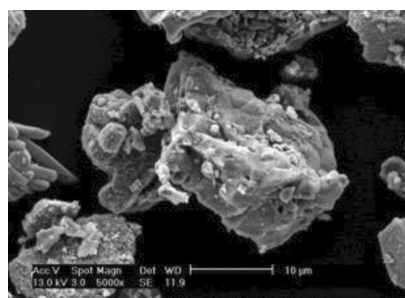
Figure 3. DTA profile of Y-Ba-Cu-O and Sm-Ba-Cu-O powder

calcined for 1 and 2 cycles were $4.28 \pm 4.15 \mu\text{m}$ and $4.67 \pm 5.54 \mu\text{m}$, respectively. For the Sm123 powders subjected to 1 calcination cycle, the average particle size was $2.37 \pm 1.77 \mu\text{m}$. A slight particle coarsening effect was observed in the Sm123 powders subjected to 2 calcination cycles, as the average particle size became $3.54 \pm 3.15 \mu\text{m}$. Particle size

distribution was exhibited in the histogram shown in Figures 6 and 7. It was evident that both the Y123 and Sm123 powders had a wide particle size distribution. The results suggest that an additional grinding step might be required to attain finer particles suitable for a subsequent fabrication process of RE123 superconducting samples.

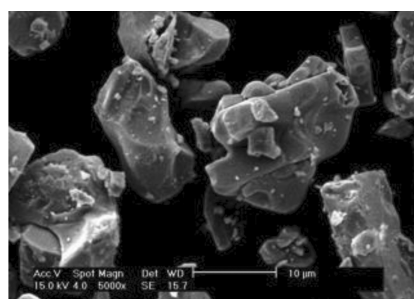


(a)

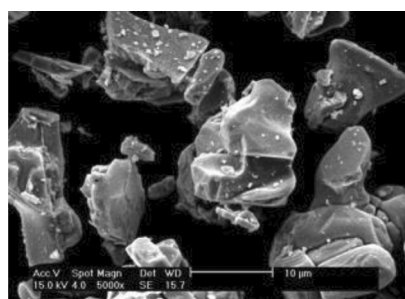


(b)

Figure 4. SEM micrographs of Y123 powders subjected to 1 (a) and 2 (b) calcination cycles



(a)



(b)

Figure 5. SEM micrographs of Sm123 powders subjected to 1 (a) and 2 (b) calcination cycles

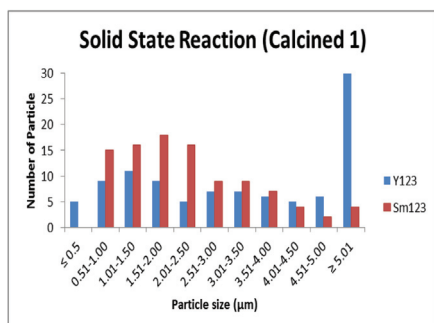


Figure 6. Histogram showing particle size distribution of Y123 and Sm123 powders subjected to 1 calcination cycle

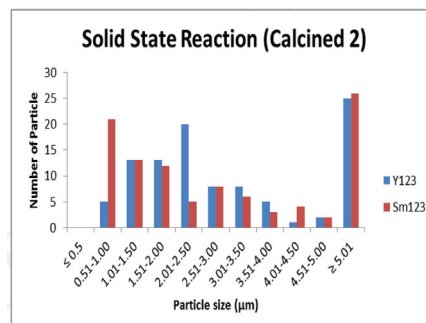


Figure 7. Histogram showing particle size distribution of Y123 and Sm123 powders subjected to 2 calcination cycles

Conclusions

YBa₂Cu₃O_{7-x}, and SmBa₂Cu_{37-x} superconducting powders with chemical compositions required for practical applications can be synthesized using the solid state reaction technique. XRD analysis indicated the desired chemical compositions, which consist of REBa₂Cu₃O_{7-x} (RE123) and RE₂BaCuO₅ (RE211). However, an insignificant quantity of impurities such as BaCO₃ and BaCuO₂ remained. The relationship between the chemical composition and thermal evolution of the RE123 powders was also investigated in this study. Results from XRD and DTA suggest that to completely eliminate the undesirable BaCO₃ phase, calcination at 920°C should be employed. Particle size analysis indicates that the powders consist of irregular-shaped particles, which were linked together in agglomerates. The sizes of most particles were in the micrometer range, with the average particle size being 4.67 μm and 3.54 μm in the Y123 and Sm123 powders, respectively. A wide distribution of particle sizes was observed in both powders. These results suggest that an additional grinding step might be required to attain fine particles suitable for a subsequent fabrication process of RE123 superconducting samples.

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