journal

J. Am. Ceram. Soc., 72 [10] 1977-79 (1989)

Reaction Sequencing During Processing of the 123 Superconductor

William J. Thomson,* Hong Wang, David B. Parkman, and Dong X. Li
Department of Chemical Engineering, Washington State University, Pullman, Washington 99164–2710

Michael Strasik and Thomas S. Luhman*
Boeing Aerospace, Seattle, Washington 98124–2207

Chan Han and Ilhan A. Aksay*
Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195

Reaction sequencing studies were conducted for two precursors to the 123 superconductor in air and helium environments. In air, the reactants in both precursor systems produce an intermediate 123 phase at 1000 K without going through the $BaCuO_2$ and Y_2BaCuO_5 intermediate phases, observed in earlier work with mixed powder precursors. In helium, the fully developed 123 tetragonal phase is formed at temperatures as low as 880 K, but it also decomposes to Y_2BaCuO_5, $BaCu_2O_2$, and $BaCuO_2$; the extent of decomposition depends on the temperature. The 123 tetragonal phase completely decomposes by 1075 K, but it can be reformed if the atmosphere is switched back to air at a temperature above 950 K. [Key words: superconductors, yttrium, barium, processing, precursors.]

THERE may be a number of reaction-kinetic paths leading to the synthesis of the $YBa_2Cu_3O_{7-x}$ ("123") superconductor. Some of these paths could lead to alternate processing routes with concomitant changes in the physical properties of the final product. For example, Rha *et al.*[1] showed that the time required for the formation of the tetragonal phase of the 123 superconductor and the subsequent sintering process could be considerably reduced if processing were conducted in an oxygen-free environment. More recently, Horowitz *et al.*[2] reported that, when an inert environment was employed, a variety of sol–gel precursors can lead to formation of the 123 phase below 1000 K, resulting in sharp T_c values and smaller grain sizes. It is also known that the 123 superconductor can be formed as thin films under processing temperatures that are below 900 K.[3,4] This temperature is in contrast with the high temperatures (~1200 K) that are needed for the conventional solid-state synthesis of 123 superconductor from Y_2O_3, CuO, and $BaCO_3$.

To date only two systematic studies have been reported on the reaction sequences that lead to the formation of the 123 superconductor during typical processing conditions. Ruckenstein *et al.*,[5] analyzing air-quenched samples with XRD, investigated the reaction pathways and kinetics for the formation of the 123 phase and found that decomposition of $BaCO_3$ was the rate-limiting step. They subsequently proposed and studied two-step procedures by forming $BaCuO_2$ in a first step to achieve rapid formation of the $YBa_2Cu_3O_{7-x}$ compound in a second step. Gadalla and Hegg[6] studied the kinetics of 123 formation using TGA and DTA analyses and concluded that the formation and decomposition of the 123 compound follow six overlapping steps that are all diffusion controlled. Both of these studies employed powder mixtures and were conducted in an oxygen-containing environment. Furthermore, Ruckenstein *et al.*[5] reported that their powders tended to agglomerate, resulting in heterogeneous product formation as a consequence of macroscopic diffusion limitations. In this paper we report on the use of in-situ dynamic XRD to follow the reaction sequences that lead to the formation of the 123 superconductor from two different precursors and under both oxygen and oxygen-free conditions. The use of dynamic XRD avoids the necessity of quenching and of the use of indirect measurements, such as mass or enthalpy changes, thereby providing unambiguous observations of the crystalline transformations as they occur.[7] In addition, the precursors were prepared to produce reactant mixing on a nanometer scale, thus minimizing the effects of mixed powder diffusion problems.

EXPERIMENTAL APPROACH

Materials

Precursors to the 123 superconductor were prepared from both citrate gels[8] and "flashed nitrates." In the former case, stoichiometric amounts of the acetates of yttrium, barium, and copper were dissolved in a mixture of citric acid and ethylene glycol, which was heated at 440 K and then diluted with distilled water. Water was gradually removed by heating the solution at 350 K. The resulting viscous solution was dried in an oven at 340 K for 2 d and then ground to a fine powder prior to experimentation via dynamic XRD. The flashed nitrate precursor was prepared by a "flashed" carbothermal reduction of the nitrate salts to produce intimately mixed Y_2O_3, CuO, and $BaCO_3$. That is, the nitrates were reduced to the oxides by exposing them to organic carbon at temperatures in excess of 900 K.

Procedures

All experiments reported here were conducted by dynamic XRD, which has been described in detail by Thomson.[9] Finely powdered samples were placed as thin beds (~100 μm thick) on an Inconel heating strip* and then subjected to various temperature–time programs under both oxygen-free and oxygen-containing (air) environments. All samples were initially heated at 5 K/min in either air or helium to 800 K, at which point a series of nonisothermal and isothermal experiments was conducted. The maximum temperature was limited to 1125 K to avoid undesirable reactions between the sample and the strip. In all cases the primary reflections of the individual species were recorded, i.e., CuO(111), $BaCO_3$(111), 123(103, 110), $BaCuO_2$(600), and $BaCu_2O_2$(103).

RESULTS

Initial XRD scans of the two pre-

D. W. Johnson — contributing editor

Manuscript No. 198390. Received May 15, 1989; approved July 17, 1989.

Supported by DARPA/AFOSR under Contract No. F49620-88-C-0143.

*Member, American Ceramic Society.

*Huntington Alloys, Inc., Huntington, WV.

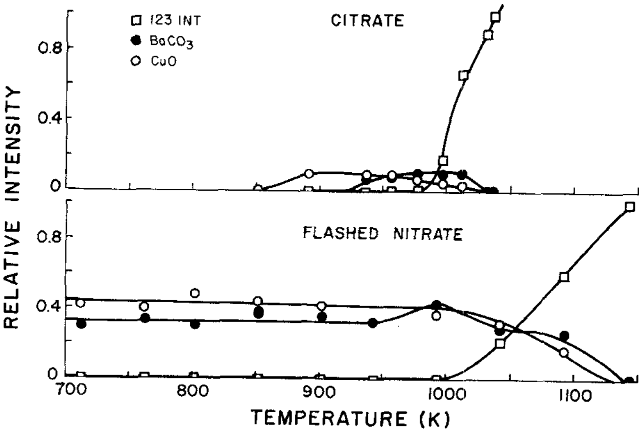

Fig. 1. Reaction sequencing for two precursors (in air, 5 K/min).

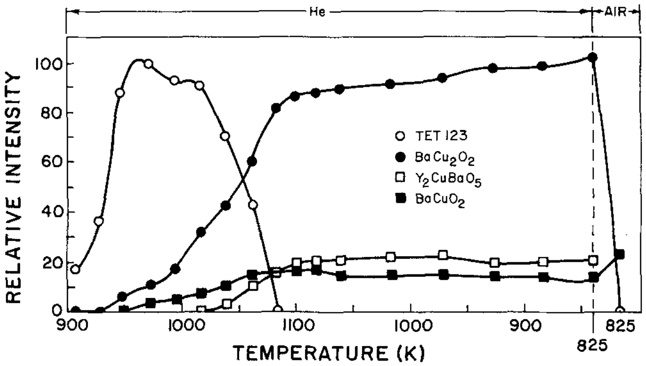

Fig. 2. High-temperature reaction sequencing of citrate gel (840 to 1100 to 825 K at 5 K/min in helium; 30 min at 825 K in air).

cursors are different in the sense that the citrate gel is completely amorphous, whereas the flashed nitrate gel exhibits a strong reflection of the rhombic phase of $BaCO_3$ and somewhat weaker reflections for both CuO and Y_2O_3. As shown (Fig. 1), with the citrate gel, there is some crystallization of the CuO and $BaCO_3$ prior to the formation of an intermediate 123 phase (labeled, "123 INT" in Fig. 1) at about 1000 K, whereas the flashed nitrate reactants remain invariant to this point. The reactivity of the citrate gel is somewhat higher, probably due to the smaller particle size of $BaCO_3$. In both these experiments, the intermediate 123 phase which is formed has a tetragonal structure, but there is no evidence of the splitting which is indicative of a fully developed 123 tetragonal phase, even under the most severe conditions employed, i.e., 1125 K for 1 h. A similar structural development was also reported by Chu and Dunn[8] in their citrate process at temperatures between 1173 and 1223 K. Similar 123 peak shapes were also observed by Kinoshita *et al.*,[10] for an oxygen-rich tetragonal 123 phase and by Okamura *et al.*,[11] and Sato *et al.*[12] for metal-deficient 123 phases. Unlike the previous reaction-sequencing work,[5,6] there is no evidence in either precursor of the presence of Y_2BaCuO_5 (the "211" phase) as an intermediate. Obviously, the reaction path is influenced by the existence of interparticle diffusion, which played a dominant role in the mixed powder systems utilized in both of the previous studies.

In contrast with the experiments conducted in air, the fully developed 123 tetragonal phase began to form from the citrate gels at temperatures as low as 890 K when a helium environment was used, provided that complete burnout of organic materials was achieved. Burnout was accomplished easily by holding the sample in air at 850 K for 10 min. Similar results were also obtained with the flashed nitrate precursor, except that the initial formation temperatures were about 60 K higher. Well-split, fully developed tetragonal peaks (103, 013, 110) were achieved within 15 min with both precursors at 1000 K, and there was no further change in the characteristics of this peak after holding for as long as 12 h. However, in none of these experiments were we able to form the fully developed orthorhombic phase when the high-temperature phases were cooled in either air or oxygen. The closest approach to fully developed orthorhombic 123 was achieved in a citrate gel run, which was heated in helium (after burnout) to 1000 K and held for 12 h before switching to air at 950 K. The room-temperature XRD scan indicated a small shoulder (013) in the major reflections (103, 110) and clear separation of secondary reflections (006, 200). Magnetic susceptibility measurements of this sample exhibited a broad T_c, starting at about 84 K.

Although it is true that an oxygen-free environment produced the tetragonal 123 phase at much lower temperatures, it rapidly decomposed to the 211 phase, as shown in the nonisothermal dynamic XRD data in Fig. 2. In fact, the 123 phase totally decomposed by 1110 K, accompanied by the formation of $BaCu_2O_2$, smaller quantities of $BaCuO_2$, and the 211 phase. This behavior was observed in both precursor systems at essentially identical temperatures. Although the formation of $BaCu_2O_2$ has been reported by Aselage and Keefer[13] as a consequence of reactions (in air) of CuO with both the 123 phase and $BaCuO_2$, it has not been observed previously as a decomposition product of the 123 phase. Further insight into this particular reaction sequence can be obtained by observing the sequencing that occurred when the environment was switched to air. When this was done at 825 K (Fig. 2), $BaCu_2O_2$ completely disappeared; the $BaCuO_2$ peaks increased; and CuO, BaO, and $BaCO_3$ formed (not shown). On the other hand, after the 123 phase had totally decomposed (at temperatures greater than 1100 K), it was found that the tetragonal 123 phase could be completely recovered whenever the environment was switched back to air at temperatures above 950 K.

DISCUSSION

The powder mixture studies by Ruckenstein *et al.*[5] and Gadalla and Hegg[6] concluded that the reaction series leading to the formation of the 123 superconductor are diffusion controlled, with $BaCuO_2$ and the 211 phase as intermediate species. However, because of the more intimate mixing of reactants in the precursor systems used in this work, diffusion lengths are reduced to nanometer dimensions, leading to lower reactant temperatures[2,8,14] and a different reaction pathway. In air we observe the formation of an intermediate species which has a tetragonal structure very similar to the tetragonal 123 phase without peak splitting at 0.275 nm (i.e., $a=b\sim c/3$). It is likely that this phase is a nonstoichiometric form of the tetragonal 123 phase with a high oxygen content where large oxygen atoms in the structure prevent the rapid diffusion required to form the fully developed tetragonal 123 phase.[10-12] This phase is not observed in an oxygen-free atmosphere because of increased atomic diffusion as a result of high oxygen vacancy concentration or an expanded lattice, as suggested by Rha *et al.*[1]

Based on the measurements conducted here, the sequential decomposition of the tetragonal 123 in an oxygen-free atmosphere appears to be

$$2YBa_2Cu_3O_{7-x} \rightarrow 2BaCu_2O_2 + BaCuO_2 + Y_2BaCuO_5 + (\tfrac{3}{2} - x)O_2 \qquad (1)$$

which is reversible at temperatures above 950 K. The presence of even small quantities of the decomposition products would explain the inability of forming fully developed orthorhombic 123 after producing the tetragonal phase in an oxygen-free atmosphere. In air atmospheres, 123 decomposition does not occur until much higher temperatures (>1275 K) and $BaCu_2O_2$ is not produced.[15] If reaction (1) goes to completion and air is not introduced until 825 K or lower (typical oxygen annealing temperatures), we would observe further decomposition, which is consistent with the following reaction sequences:

$$BaCu_2O_2+\tfrac{1}{2}O_2 \rightarrow BaCuO_2+CuO \qquad (2)$$

$$BaCuO_2 \rightarrow BaO+CuO \qquad (3)$$

$$BaO+CO_2 \rightarrow BaCO_3 \qquad (4)$$

The successful route to formation of the orthorhombic 123 phase via oxygen-free calcination at lower temperatures is dependent on the ability to reverse reaction (1), which can only be achieved by switching to air at temperatures above 950 K.

REFERENCES

[1] J. J. Rha, K. J. Yoon, S. L. Kang, and D. N. Yoon, "Rapid Calcination and Sintering of $YBa_2Cu_3O_x$ Superconductor Powder Mixture in Inert Atmosphere," *J. Am. Ceram. Soc.*, **71** [7] C-328–C-329 (1988).

[2] H. S. Horowitz, S. J. McLain, A. W. Sleight, J. D. Druliner, P. L. Gai, M. J. VanKavelaar, J. L. Wagner, B. D. Biggs, and S. J. Poon, "Submicrometer Superconducting $YBa_2Cu_3O_{6-x}$ Particles Made by Low-Temperature Synthetic Route," *Science (Washington)*, **243**, 66–69 (1989).

[3] X. D. Wu, A. Inam, T. Venkatesan, C. C. Chang, E. W. Chase, P. Barboux, J. M. Tarascon, and B. Wilkens, "Low-Temperature Preparation of High-T_c Superconducting Thin Films," *Appl. Phys. Lett.*, **52** [9] 754–56 (1988).

[4] T. Miura, Y. Terashima, M. Sagoi, and K. Kubo, "Low-Temperature Preparation of As-Sputtered Superconducting YBaCuO Thin Films by Magnetron Sputtering," *Jpn. J. Appl. Phys.*, **27** [7] L1260–L1261 (1988).

[5] E. Ruckenstein, S. Narain, and N. L. Wu, "Reaction Pathways for the Formation of the $YBa_2Cu_3O_{7-x}$ Compound," *J. Mater. Res.*, **4** [2] 267–72 (1989).

[6] A. Gadalla and T. Hegg, "Kinetics and Reaction Mechanisms for Formation and Decomposition of $Ba_2YCu_3O_x$," *Thermochim. Acta*, **145**, 149–63 (1989).

[7] H. Wang, D. X. Li, and W. J. Thomson, "Transition Temperatures for the Tetragonal–Orthorhombic Phase Transition in the 123 Superconductor," *J. Am. Ceram. Soc.*, **71** [11] C-463–C-465 (1988).

[8] C. T. Chu and B. Dunn, "Preparation of High-T_c Superconducting Oxides by the Amorphous Citrate Process," *J. Am. Ceram. Soc.*, **70** [12] C-375–C-377 (1987).

[9] W. J. Thomson, "Dynamic X-ray Diffraction: A Technique for Following Solid-State Reactions"; to be published in Ceramic Transactions, Vol. 5, Advanced Characterization Techniques for Ceramics. Edited by W. S. Young, G. L. McVay, and G. E. Pike. American Ceramic Society, Westerville, OH, 1989.

[10] K. Kinoshita, A. Matsuda, T. Ishii, N. Suzuki, H. Shibata, T. Watanabe, and T. Yamada, "Preparation and Superconducting Properties of Tetragonal $Ba_2YCu_3O_{7-y}$ and $Ba_2EuCu_3O_{7-y}$ with Low Oxygen-Defect Concentration ($0.05<y<0.20$)," *Jpn. J. Appl. Phys.*, **27** [5] L795–L798 (1988).

[11] F. P. Okamura, S. Sueno, I. Nakai, and A. Ono, "Crystal Structure of $Ba_2YCu_{3-x}O_{7-y}$, A Superconductive Compound Determined by X-ray Single-Crystal Diffraction Method," *Mater. Res. Bull.*, **22**, 1081–85 (1987).

[12] S. Sato, I. Nakada, T. Kohara, and Y. Oda, "Crystal Structure of Superconductor $Ba_2YCu_{2.89}O_{6.80}$," *Jpn. J. Appl. Phys.*, **26** [5] L663–L664 (1987).

[13] T. Aselage and K. Keefer, "Liquidus Relations in Y-Ba-Cu Oxides," *J. Mater. Res.*, **3** [6] 1279–91 (1988).

[14] P. Ravindranathan, S. Komarneni, A. Bhalla, R. Roy, and L. E. Cross, "Sol–Gel Synthesis of Fine-Particle Superconducting Oxide, $YBa_2Cu_3O_{7-x}$," *J. Mater. Res.*, **3** [5] 810–12 (1988).

[15] H. J. Scheel and F. Licci, "Crystal Growth of High-Temperature Superconductors," *MRS Bull.*, [10] 56–60 (1988). □