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# Synthesis of High-$T_c$ $YBa_2Cu_3O_{7-x}$ Superconductors at a Low Annealing Temperature from a Glass Precursor

H. S. KOO[†,††], T. Y. TSENG[††], R. S. LIU[†],
Y. T. HUANG[†], K. S. KUAN[†] and P. T. WU[†]

[†]*Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 31015, Taiwan, R.O.C.*
[††]*Institute of Electronics, National Chiao-Tung University, Hsinchu, Taiwan, R.O.C.*

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High-$T_c$ superconducting $YBa_2Cu_3O_{7-x}$ oxides prepared at a low annealing temperature (850°C) from a glass precursor by rapid quenching from the melt have been successfully obtained with zero resistivity at the temperature of 92 K. The kinetics of the phase transition from the glassy state to superconducting phase have been characterized by differential thermal analysis, X-ray diffraction and scanning electron microscopy. The magentic properties of the $YBa_2Cu_3O_{7-x}$ samples were measured by dc SQUID magnetometer are also discussed.

**KEYWORDS:** high-$T_c$ superconducting oxide, glass precursor, rapid quenching, phase transition, dc SQUID

## §1. Introduction

Since Bednorz and Müller[1)] discovered that an oxygen-deficient perovskite oxide with a critical superconducting transition temperature, $T_c$, near 30 K, which was higher than any ever found before,[2)] existed in the Ba–La–Cu–O system, numerous studies on this novel and promising superconducting material spread all over the world. Similar systems with higher-$T_c$ superconducting oxides, such as Y–Ba–Cu–O, Bi–Sr–Ca–Cu–O and Tl–Ba–Ca–Cu–O, have consequently been discovered by Wu *et al.*,[3)] Maeda *et al.*[4)] and Sheng and Hermann,[5)] respectively. In spite of the many attempts that have been made to synthesize and characterize the superconducting phase using different experimental processes, many problems still have not been solved. Therefore, new material systems, new processes and optimized process conditions for high-$T_c$ superconductors are being actively explored to raise critical temperature and critical current density.

It is well known that the physical properties of the superconducting oxides strongly depend on the processes and process conditions; therefore, different results are obtained from different processes and process conditions. The superconducting oxides are generally prepared through the sintering method, but they are usually porous. It is well known that the rapid-quench technique[6)] is a mature process for metal production (metallic glass) and has the advantages of fine microstructures, reduced segregation, extended solid solubility, prepared particular shapes, and the formation of new types of phases. Recently, some research groups[7-10)] attempted to use this method for the preparation of superconducting oxides, but their information was rather limited.

In this paper, we systematically investigated further optimized process conditions for the preparation of high-$T_c$ superconducting $YBa_2Cu_3O_{7-x}$ (hereafter referred to as YBCO) oxides through the rapid-quench method. The as-quenched and annealed (in flowing oxygen) samples were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Superconductivity of samples was examined both resistively and magnetically. The present results showed that a lower annealing temperature process (<900°C) could transform the amorphous as-quenched sample into the superconducting YBCO phase with a $T_c$ above 90 K.

## §2. Experimental Procedure

High-purity powders of $Y_2O_3$ (99.9%), $BaCO_3$ (99.9%) and CuO (99.9%) with a cation ratio of Y:Ba:Cu = 1:2:3 were well mixed using an agate mortar and pestle. The mixed powder was calcined at 920°C for 10 hours in air and cooled down to room temperature at a cooling rate of 5°C/min. This calcination procedure was repeated two more times to assure compositional homogeneity. To prepare the specimens for rapid-quench processing, the calcined powders were pressed into a long-plate shape ($40 \times 10 \times 3$ mm$^3$) with a pressure of 0.5 ton/cm$^2$. A high-temperature (1800°C) $H_2$–$O_2$ torch was used to melt these specimens. Firstly, the bottom of the long-plate specimen was moved to the high-temperature region of the $H_2$–$O_2$ flame and was rapidly melted in several seconds. Secondly, molten droplets with diameters of about 3 mm were dropped gravitationally onto the stainless steel plate to form films 0.5–1 mm thick.

As-quenched samples were then annealed at various temperatures (800°C, 850°C and 950°C) for 12 hours in flowing oxygen. X-ray powder diffraction patterns of the samples were obtained using a Philips PW1700 diffractometer with nickel-filtered Cu K$\alpha$ radiation. The surface morphology and thermal characteristics of the samples were examined using a Hitachi SEM and Dupont 1090 DTA, respectively. A standard four-probe technique was employed for the resistivity measurement. Electrical contacts to the samples were made by fine copper wires attached to the samples with a conductive paint. The temperature was measured with a platinum resistor close to the sample. The resistance limit measured was $10^{-6}\,\Omega$. Magnetic susceptibility measurements were performed in a superconducting quantum interference device (SQUID, Quantum Design).

## §3. Results and Discussion

Figure 1 shows X-ray diffraction patterns of $YBa_2Cu_3O_{7-x}$ ceramics sintered at the temperature of 950°C for 10 hours in flowing oxygen (a), an as-quenched sample made by the rapid-quench method (b) and annealed samples which were heat-treated at various temperatures (c)–(e). Figure 1(a) shows a sintered sample with orthorhombic structure of the high-$T_c$ superconducting $YBa_2Cu_3O_{7-x}$ phase, as indicated by specific reflection indices. The XRD pattern of the as-quenched sample shown in Fig. 1(b) indicates that the as-quenched sample consists of the amorphous phase, which has no apparent peaks in the XRD pattern. Komatsu[11] mentioned that crystalline phases of $BaCuO_2$ and $Y_2O_3$, which had apparent peaks in the XRD pattern, existed in the quenched sample. The present data show no extra peak for the as-quenched sample. This may be due to the differences in the raw material (it was sufficiently calcined for the present test) and the method of melting.

The XRD patterns of as-quenched samples annealed at 800°C, 850°C and 950°C for 12 hours in flowing oxygen are shown in Figs. 1(c)–1(e), respectively. The pattern (c) obtained for the as-quenched sample annealed at 800°C for 12 hours in flowing oxygen indicates a trace amount of peaks and may represent the crystalline phase of $BaCuO_2$, CuO and $Y_2O_3$.[11] This also indicates that crystallization occurred in the sample annealed at around 800°C, as proved by the SEM photograph (Fig. 2). Figure 1 also shows that the crystallinity of the annealed samples is increased with increasing annealing temperatures. The XRD patterns of samples annealed at 850°C (d) and 950°C (e) are almost identical to those of the standard sintered samples, which exhibit an orthorhombic structure, as indexed by specific reflection. The results show that the orthorhombic structure of the high-$T_c$ superconducting phase can be obtained by annealing the as-quenched sample at a lower temperature(850°C), but the general result is that it is obtained at a higher temperature (950°C) for the solid-state sintering method.

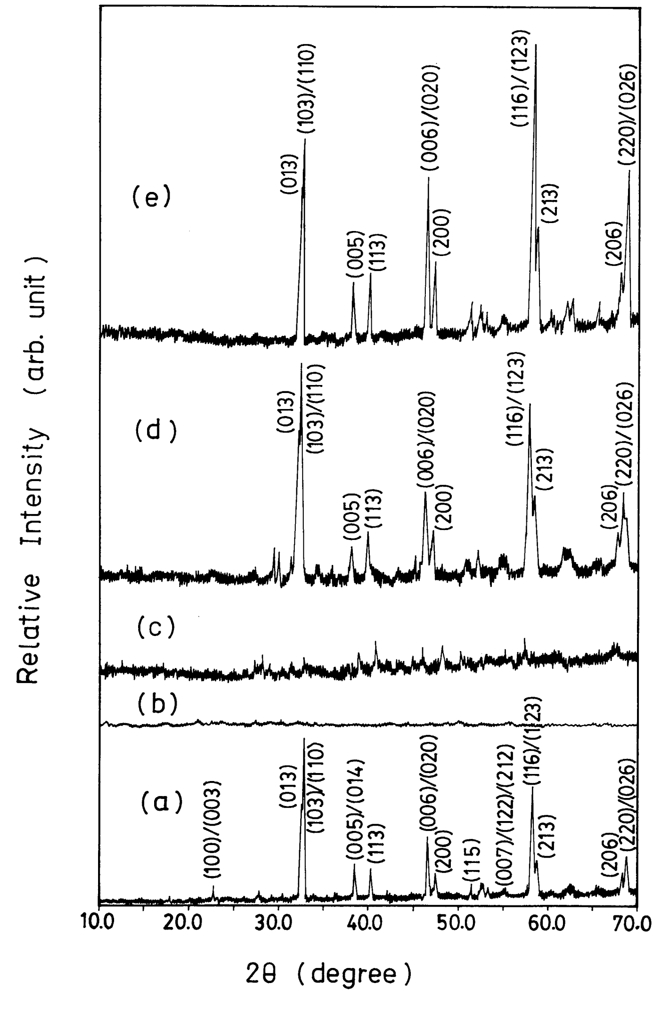


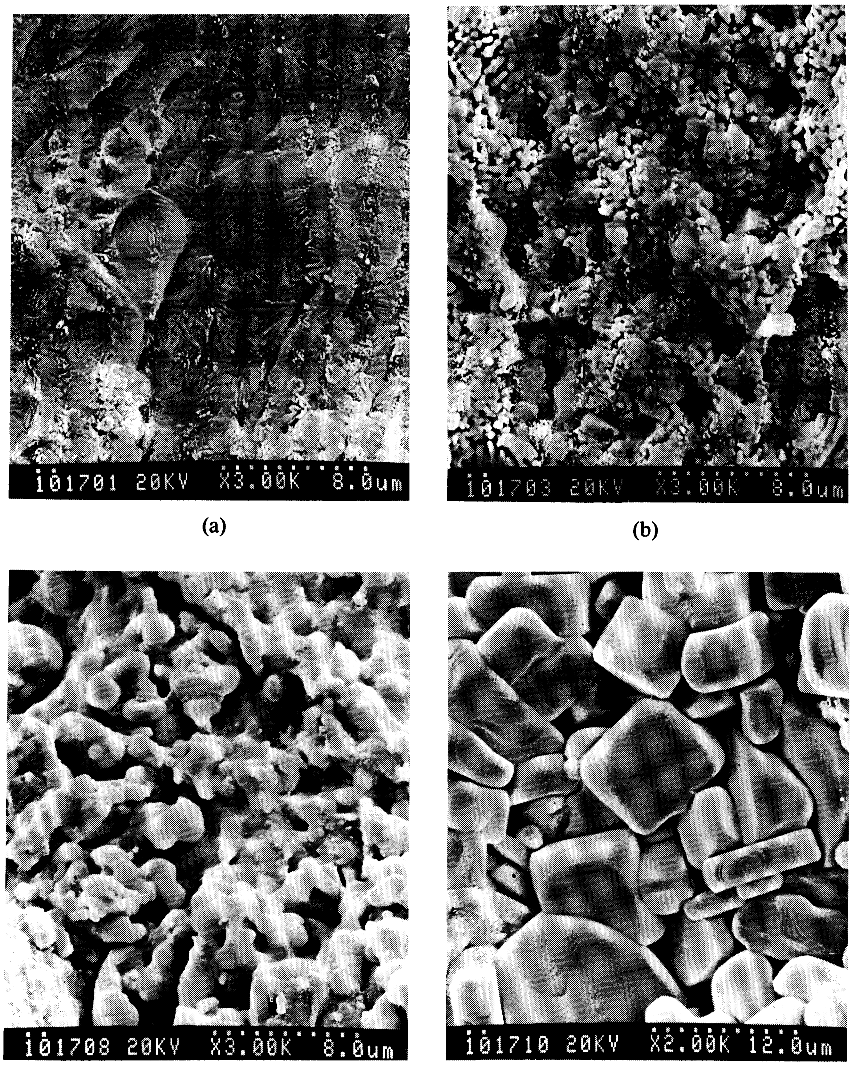
Fig. 1. X-ray diffraction patterns of the sintered sample (a), the as-quenched sample (b), and the annealed samples heat-treated at 800°C (c), 850°C (d) and 950°C (e).

Figure 2 shows scanning electron microscopy photographs of the fracture surfaces of the as-quenched (a) and the annealed samples (b)–(d). The as-quenched sample has a denser and flockier surface, which is expected for amorphous materials. On the other hand, the surface of the sample annealed at 800°C consists of grains of a few microns. As the annealing temperature increased from 800°C to 950°C, the grain sizes were also increased and a square structure was randomly developed.

Figure 3(a) shows differential thermal analysis (DTA) curves in an $O_2$ atmosphere for the as-quenched sample. Four endothermic peaks were observed at about 300°C, 860°C, 920°C and 950°C. The endothermic peak at 950°C was confirmed to represent the melting of the sample, while the peaks at 860°C and 920°C might be due to a reaction product of $BaCuO_2$, CuO, and the formation of the liquid phase, respectively. The glass transition temperature and the crystallization temperature were identified as 330°C and 780°C, respectively.

The DTA curve shown in Fig. 3(b) indicates that the sample annealed at 800°C still retains certain compounds, such as $BaCuO_2$ and CuO, as evidenced by the phase diagram.[12] Hence, in addition to the melting peak observed at about 950°C, two endothermic peaks are also observed at about 860°C and 940°C. This result is partly the same as that in Fig. 3(a). In Fig. 3(b), the glass transition peak and the crystallization peak are not shown in the DTA curve for the sample annealed at 800°C. Therefore, the crystallization reaction, which was examined by DTA and SEM, is confirmed to occur at about 800°C. Figures 3(c) and 3(d) show the DTA curves of the samples annealed at 850°C and 950°C. In these two DTA curves, only one endothermic peak was observed, at about 950°C. This endothermic peak may be attributed to the melting of a single phase, which was examined as the orthorhombic $YBa_2Cu_3O_{7-x}$ phase by XRD.

Figure 4 shows normalized electrical resistance (R/R300K) as a function of temperature for the samples annealed in the temperature range from 800°C to 950°C for 12 hours in flowing oxygen. The as-quenched sample never showed superconductivity in a cryostat. The as-quenched samples were annealed in the appropriate temperature range superconductivity was exhibited in the annealed samples. With decreasing temperature, the electrical resistance of the annealed samples decreased almost linearly in the range of 300 K to 100 K and ex-



(a) (b)

(c) (d)

Fig. 2. Scanning electron microscopy photographs of the fracture surfaces of as-quenched (a) and annealed samples heat-treated at 800°C (b), 850°C (c) and 950°C (d).

hibited a minimum electrical resistance value at about 95 K. The electrical resistance at 95 K decreased significantly with further decrease in the temperature and zero resistance was achieved in the temperature range of 90–92 K, except for in the sample annealed at 800°C.

The magnetic measurments were carried out on a quantum design magnetic properties measurement system. The magnetization was measured by the following procedure: The samples were cooled to 6 K in a zero field. At a low temperature, a 200-gauss field was applied. The magnetization was measured while the temperature was increased (ZFC). With the field still on, the sample was cooled from room temperature to 6 K. The magnetization was measured while the temperature was decreased (F.C.).

Figure 5 exhibits both ZFC and FC magnetization data ($4\pi M/H$) for various samples annealed at different temperatures. The diamagnetism of the sample annealed at 800°C for 12 hours is weak. However, the flux exclusion and expulsion for the sample annealed at 850°C for 12 hours are relatively high: 60% and 20% volume fractions at 6 K. Samples annealed at 850°C for 12 hours do not show a significant improvement: 60% and 16% volume fractions. In spite of the different annealing temperatures, the $T_c$ onsets of the samples are about the same, around 90 K, which is consistent with the resistivity data.

In conclusion, a high-$T_c$ superconducting $Y_2Ba_2Cu_3O_{7-x}$ phase with zero resistivity at about 92 K was successfully prepared by annealing the as-quenched sample at a lower temperature (850°C) than in the usual sintering process. The XRD and DTA results showed that crystallization occurred at about 800°C, while the superconducting phase with $T_c$ above 90 K was formed at 850°C. The magnetic and electrical resistance measurements also showed the same onset temperature, at about 95 K, for the samples annealed at 850°C and 950°C. The kinetics of the phase transition from the glassy state to the superconducting phase depended not only on the annealing temperature but also on the annealing time. A more detailed study on the reaction mechanism of the high-$T_c$ superconducting phase is in progress.

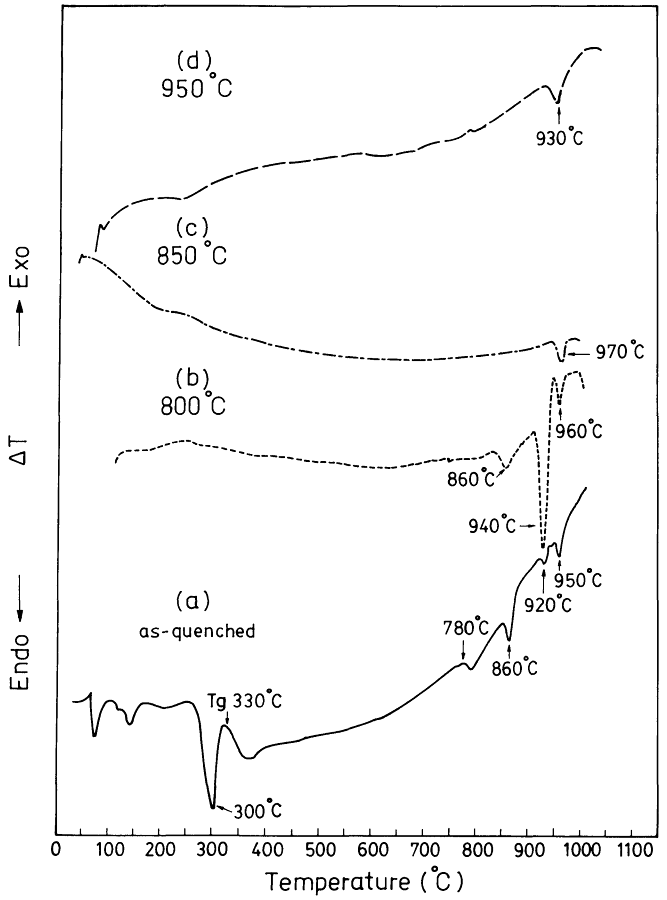


Fig. 3. DTA Curves in an $O_2$ atmosphere for as-quenched and annealed samples heat-treated at various temperatures.

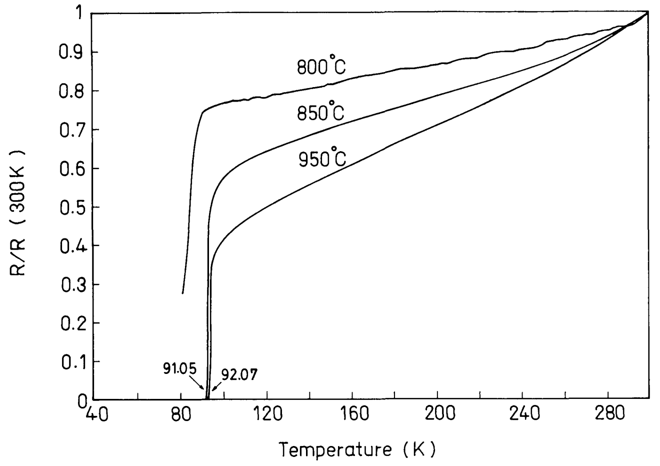


Fig. 4. Normalized resistance vs temperature curves for annealed samples heat-treated at various temperatures.

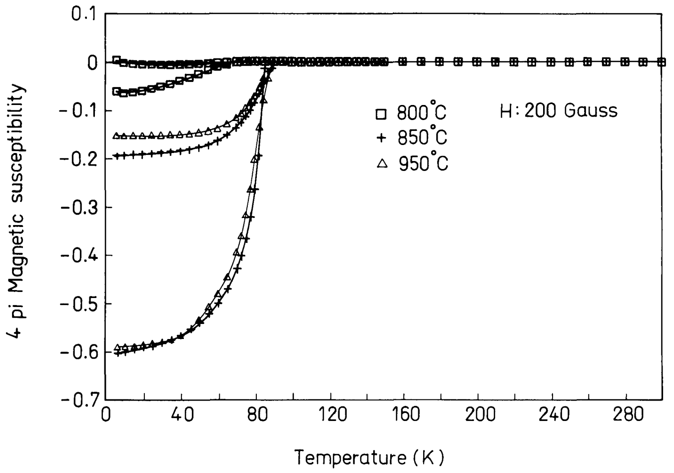


Fig. 5. Magnetic susceptibility vs temperature curves for annealed samples heat-treated at various temperatures.

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