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Preparation of $YBa_2Cu_3O_{7-\delta}$ Superconductor through Organometallic Route

Shin-ichi HIRANO, Takashi HAYASHI, Ronald H. BANEY,
Masashi MIURA, and Hiroyuki TOMONAGA
Department of Applied Chemistry, Faculty of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464

The preparation of high Tc superconducting $YBa_2Cu_3O_{7-\delta}$ compound was investigated through organometallic route, using Ba metal, $Y(O\text{-}iPr)_3$ and Cu-alkoxides or Cu-acetylacetonate as starting materials. Chemically homogeneous submicron powder of orthorhombic $YBa_2Cu_3O_{7-\delta}$ was prepared as a single phase by controlled partial hydrolysis of metal alkoxides. It was confirmed by dc resistivity and magnetic susceptibility measurements that single phase $YBa_2Cu_3O_{7-\delta}$ ceramics exhibited superconductivity at about 90 K (Tc onset).

Recently, intensive studies on the preparation of high Tc $YBa_2Cu_3O_{7-\delta}$ superconductor have been reported.[1] So far, the superconducting $YBa_2Cu_3O_{7-\delta}$ compound has been usually prepared by the conventional solid state reaction between Y_2O_3, $BaCO_3$, and CuO. It is, however, difficult to prepare chemically homogeneous, highly pure, fine particles by the solid state reaction method and to control sufficiently the particle size and morphology for the fabrication of dense ceramics on sintering. Therefore, the alternative chemical routes such as the coprecipitation of nitrates[2,3] and the pyrolysis of organic acid salts[4,5] have currently receieved great attention, which will allow the precipitation of chemically more homogeneous fine particles. Although the chemical route affords the highly pure and homogeneous particles and more controllable processing, there are, however, some difficulties of non-uniform and incomplete precipitation, contamination from precipitating agents, heterogeneous segregation due to the difference in the decomposition temperatures of organic acid salts and the easier formation of $BaCO_3$ involving in the pyrolysis process of larger organic groups.

In this work, we report the preparation of the $YBa_2Cu_3O_{7-\delta}$ superconductor through organometallic route with metal alkoxides and acetylacetonates which may offer many advantages as follows; high homogeneity, high purity, lower temperature processing and possibility of the formation of films and fibers by controlling the viscosity of solution. The basic experiments were focussed on the selection of some organometallic compounds and metal alkoxides as starting materials and suitable solvents to prepare chemical homogeneous solution, and the processing and firing conditions to prepare fine powders of orthorhombic $YBa_2Cu_3O_{7-\delta}$ compound.

$Y(O\text{-}iPr)_3$ (3N) and high pure Ba metal (4N) were used as starting materials. $Cu(OEt)_2$, $Cu(OC_2H_4OC_2H_5)_2$, $Cu(acac)_2$, and Cu-stearate with chemical pure grade

were used as Cu-compounds. $Cu(OEt)_2$ was found to be insoluble in common organic solvents except amine and acetylacetone solvents. Cu-stearate was soluble in toluene, pyridine and acetylacetone solvents, while these solvents were not suitable for Y- and Ba-compounds. Thus, $Cu(acac)_2$ and $Cu(OC_2H_4OC_2H_5)_2$ were selected as starting materials. 2-Methoxy and 2-ethoxy ethanol were found to be the most suitable solvents among common organic solvents for these starting materials.

The starting materials were dissolved in absolute 2-methoxy or 2-ethoxy ethanol in the stoichiometric composition with Y : Ba : Cu = 1 : 2 : 3. The solution was stirred in dry nitrogen and heated up to 60 °C for 12 h. Then, the solution was hydrolyzed by the slow addition of the desired amount of water diluted with solvent. After stirring and heating continued for several hours, the solution was evaporated with stirring under vacuum at about 60 °C, resulting in a amorphous powder precursor. The powder was calcined in flowing O_2 at temperatures between 800 and 950 °C for times up to 24 h. The calcined powder was die-pressed and sintered in flowing O_2 at temperatures up to 920 °C, followed by the annealing at temperatures between 450 and 550 °C.

Figure 1 shows DTA-TG curves of as-prepared specimens by the hydrolysis of Y-, Ba-, and Cu-alkoxides. Two exothermic peaks with gradual weight loss were

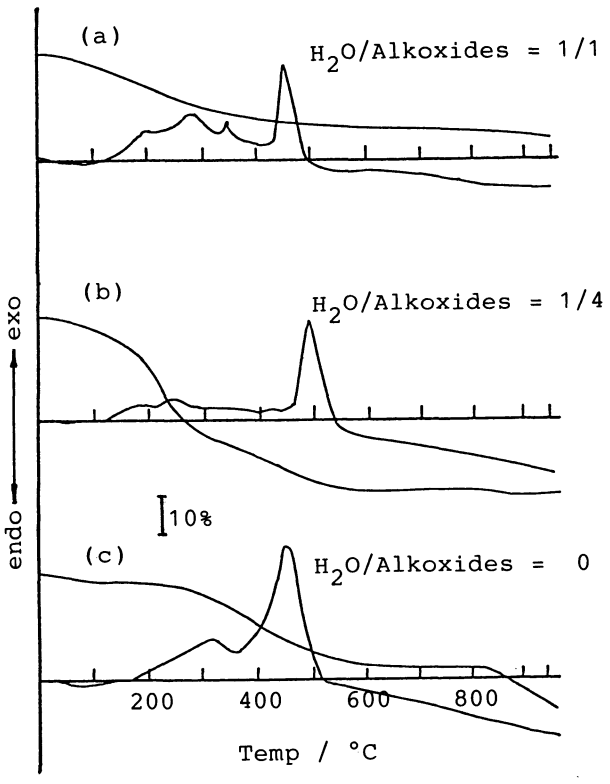

Fig. 1. DTA and TG curves of specimens prepared by the hydrolysis of Y-, Ba-, Cu-alkoxides.

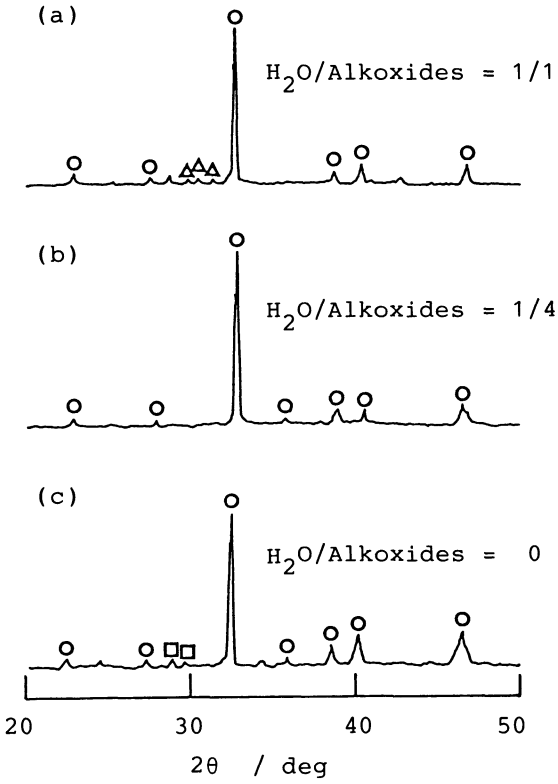

Fig. 2. X-Ray diffraction patterns of $YBa_2Cu_3O_{7-\delta}$ powders calcined at 900 (a) and 850 °C (b),(c).
○:$YBa_2Cu_3O_{7-\delta}$, △:Y_2BaCuO_5
□:$BaCuO_2$

observed in all specimens between 200 and 300 °C, and between 400 and 500 °C, which correspond to the thermal decomposition and the oxidation of organic groups. In the specimens prepared by the hydrolysis of the metal alkoxides, less-detectable weight loss was observed above 600 °C, while large weight loss was observed above 800 °C in the specimen prepared without any water addition (no-hydrolysis). The large weight loss corresponds to the decomposition of $BaCO_3$ formed during heating by the reaction of barium compound with carbonaous residue derived from organic groups.

Figure 2 shows X-ray powder diffraction patterns of the powders calcined at 850 °C for 12 h and 900 °C for 7 h, followed by the annealing between 450 and 550 °C in O_2 flow. In the powders prepared by the hydrolysis of metal alkoxides with the equivalent amount of water and without any water addition, $BaCuO_2$ and Y_2BaCuO_5 were formed along with $YBa_2Cu_3O_{7-\delta}$. On the other hand, chemically homogeneous submicron powders of orthorhombic $YBa_2Cu_3O_{7-\delta}$ could be prepared at 850 °C as a single phase by controlled partial hydrolysis of metal alkoxides with the addition of water less than the equilivalent amount.

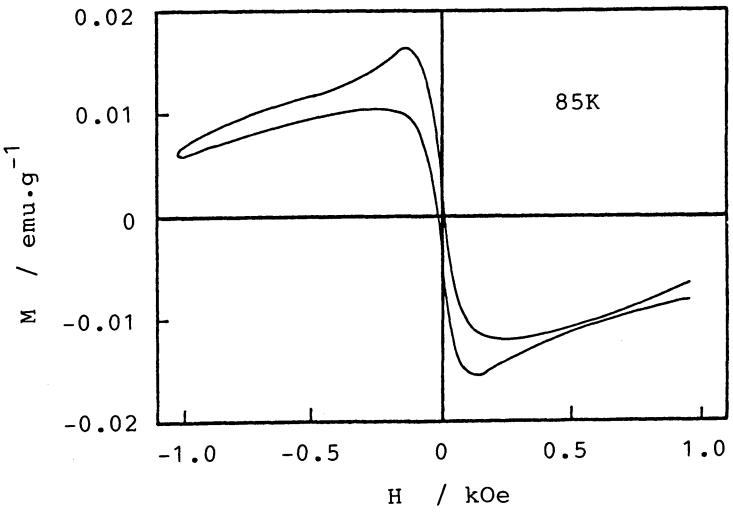

Fig. 3. Magnetization vs. magnetic field for $YBa_2Cu_3O_{7-\delta}$ calcined powder.

The superconducting-state magnetization, Ms(H), of fine powders obtained with a magnetic balance, is shown for 85 K in Fig. 3. The hysteresis exists in the Ms(H) curves between increasing and decreasing the magnetic field (H), which is caused by the trap of magnetic flux. The lower critical field H_{c1} is found to be about 0.2 kOe at 85 K and the susceptibility is about -0.016 emu/g.

The dc resisistivity of $YBa_2Cu_3O_{7-\delta}$ sintered bodies was measured by the four probe method with indium contact electrodes. As shown in Fig. 4, the superconducting transition starts

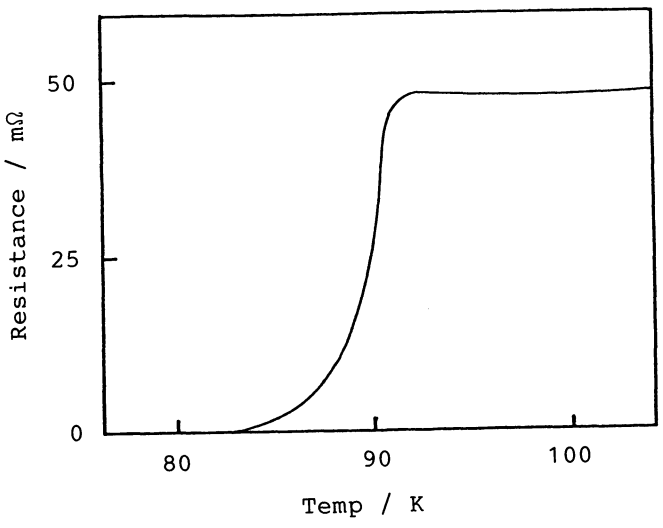

Fig. 4. Temperature dependence of the resistance of the $YBa_2Cu_3O_{7-\delta}$ sintered body at 920 °C.

at about 90 K and the resistance becomes zero at about 80 K. Figure 5 shows the fracture surface of the $YBa_2Cu_3O_{7-\delta}$ sintered body. The microstructure consisted of uniform grains of 2-3 μm.

The detailed research is in progress to confirm the processing of the films and fibers of $YBa_2Cu_3O_{7-\delta}$ at lower temperatures.

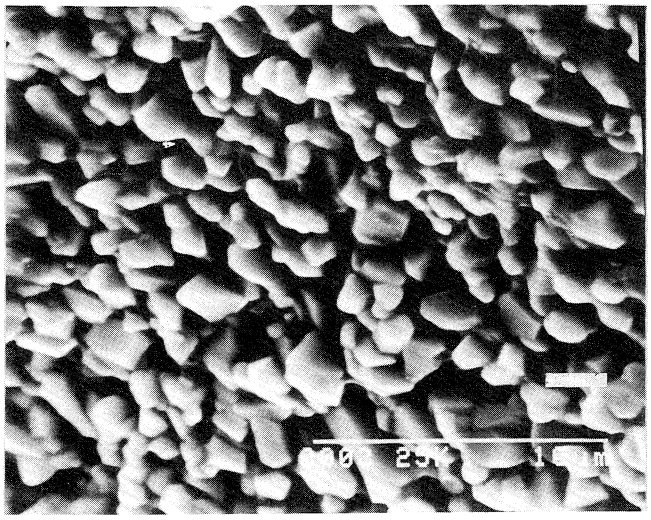

Fig. 5. SEM photograph of the fracture surface of $YBa_2Cu_3O_{7-\delta}$ sintered body.

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