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Synthesis of $Ba_2YCu_3O_{7-\delta}$ Superconductor through Organometallic Route

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The chemical synthesis of a high-T_c $Ba_2YCu_3O_{7-\delta}$ superconductor was investigated through the organometallic route, using Ba metal, $Y(OPr^i)_3$, and Cu-alkoxides or Cu-acetylacetonate as starting materials. Chemically homogeneous submicron powders of single phase $Ba_2YCu_3O_{7-\delta}$ were successfully prepared at 750 °C by controlled partial hydrolysis of metal alkoxides. The utilization of ozone for favorable decomposition of $Ba_2YCu_3O_{7-\delta}$ precursors was found to have a remarkable effect on suppressing the formation of $BaCO_3$ and lowering the formation temperature of $Ba_2YCu_3O_{7-\delta}$ to about 650 °C. The single phase $Ba_2YCu_3O_{7-\delta}$ ceramics exhibited superconductivity at approximately 83 K (T_c end).

Recently, intensive studies on the preparation of high-T_c $Ba_2YCu_3O_{7-\delta}$ superconductor have been performed.[1] The superconducting $Ba_2YCu_3O_{7-\delta}$ compound has been usually prepared by the conventional solid-state reaction between Y_2O_3, $BaCO_3$, and CuO and sintering at 950 °C, followed by slow cooling in the range of 350—650 °C. It is, however, difficult to prepare chemically homogeneous, highly pure fine particles by the solid state reaction and to control the particle size and morphology suitable for the fabrication of dense ceramics on sintering. Therefore, the alternative chemical routes such as coprecipitation of nitrates with oxalate[2,3] and citrate,[4] pyrolysis of organic acid salts,[5,6] and spray pyrolysis of nitrate solution[7] have currently received particular attention. These procedures may allow the synthesis of more chemically homogeneous fine particles. Although the chemical route affords highly pure and homogeneous particles and more controllable processing, there are some difficulties: non-uniform and incomplete precipitation, contamination by precipitating agents, and heterogeneous segregation due to the difference in decomposition temperatures of organic acid salts. Furthermore, another unavoidable problem encountered in the chemical route is the formation of $BaCO_3$ during calcination of the powder precursors, resulting easily in heterogeneous phase separation and, thereby, the formation of secondary phases such as $BaCuO_2$, Y_2O_3, Y_2BaCuO_5, etc. In particular, pyrolytic process of organic acid salts involves easier formation of $BaCO_3$.

The sol-gel method using alkoxides generally offers possibility of formation of films and fibers by controlling the solution viscosity as well as of high homogeneity, high purity, and lower temperature processing.

In a preceding work,[8] we reported the preparation of $Ba_2YCu_3O_{7-\delta}$ superconductor through an organometallic route with metal alkoxides and acetylacetonates. The preliminary experiments were tried to select organometallic compound and metal alkoxide as starting materials and appropriate solvent to prepare homogeneous solution. However, the calcination conditions to prepare $Ba_2YCu_3O_{7-\delta}$ powders at temperatures as low as possible have not fully optimized and the influence of firing atmosphere on the formation of $Ba_2YCu_3O_{7-\delta}$ compound has not been clarified. The present paper describes the selection of Cu-compound and solvent, a newly developed preparation process of chemically homogeneous solution, and calcination conditions to prepare fine powders of orthorhombic $Ba_2YCu_3O_{7-\delta}$ compound at temperatures as low as possible.

Experimental

The use of cupric organometallic compounds as starting materials is limited due to low solubility in common organic solvents. In the present work, $Cu(OEt)_2$, $Cu(OC_2H_4OEt)_2$, $Cu(acac)_2$, and $Cu(C_{17}H_{35}COO)_2$ with chemical-pure grade were examined as the source of Cu-compounds. The solubility of each Cu-compound in various organic solvents is compared in Table 1. $Cu(OEt)_2$ was found to be insoluble in organic solvents except amine and acetylacetone which tend to form readily coordination compounds with Cu-compounds. $Cu(C_{17}H_{35}COO)_2$ was soluble in toluene, pyridine, and acetylacetone, while these solvents were not suitable for $Y(OPr^i)_3$ and $Ba(OPr^i)_2$. $Cu(acac)_2$ was soluble in 2-methoxy-and 2-ethoxyethanol. $Cu(OC_2H_4OEt)_2$ was soluble in 2-ethoxyethanol, THF, and amine solvents. Thus, $Cu(acac)_2$ and $Cu(OC_2H_4OEt)_2$ were selected as starting materials. 2-Methoxy- and 2-ethoxyethanol were the most suitable solvents among common organic solvents for these starting materials.

Figure 1 shows the flowchart for chemical processing of $Ba_2YCu_3O_{7-\delta}$ superconductors through the organometallic route. $Y(OPr^i)_3$ (purity 99.9%) and high-pure Ba metal (purity 99.99%), which are soluble in common organic solvents, were used as starting materials.

The starting materials were dissolved in absolute 2-ethoxyethanol in the stoichiometric composition of Ba:Y:Cu=2:1:3. The initial concentration of alkoxides was 0.005 mol l^{-1}. The solution was stirred in dry nitrogen and heated at 40 °C for 12 h. Then, the solution was hydrolyzed by slow addition of desired amount of water diluted with solvent (1:10 volume ratio). The molar ratio of water to the sum of Ba-, Y-, and Cu-alkoxides was 1/4 and 1 (the theoretically required amount). After stirring and heating for several hours, the solution was evaporated with stirring

Table 1. Solubility of Cupric Organometallic Compounds[a)]

Solvents	$Cu(Sta)_2$	$Cu(OEt)_2$	$Cu(OR)_2$[b)]	$Cu(acac)_2$
Hexane	—	×	—	—
Toluene	○	×	—	—
Triethylamine	—	×	—	—
Diethylamine	—	○	○	—
Diisopropylamine	—	×	—	—
Ethylene glycol dimethyl ether	×	—	×	×
Tetrahydrofuran	—	×	○	—
Pyridine	○	—	—	—
2-Methoxyethanol	×	—	×	○
1-Propanol	—	×	—	—
2-Propanol	×	×	—	×
Ethanol	—	×	—	×
Acetylacetone	○	○	—	×
2-Ethoxyethanol	—	—	○	○
Diethylene glycol	—	—	—	×
Methanol	—	—	×	—
2-Aminoethanol	—	○	—	—
Ethylene glycol	—	—	—	—
Hexamethyldisiloxane	×	—	—	—
Dimethyl sulfoxide	×	×	—	—
N,*N*-Dimethylformamide	×	×	—	—

a) ○; soluble, ×; insoluble or sparingly soluble. b) $R=C_2H_4OC_2H_5$.

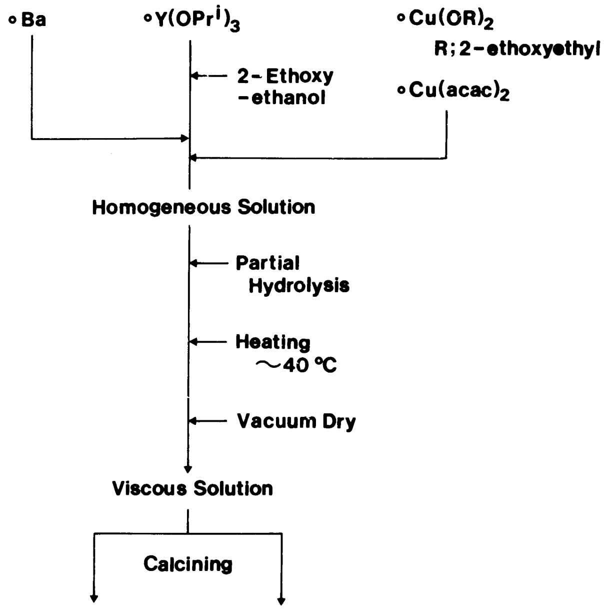

Fig. 1. The flowchart for chemical processing of $Ba_2YCu_3O_{7-\delta}$ through organometallic route.

under vacuum at about 40 °C to give an amorphous powder precursor. The powder was calcined in flowing O_2 or O_2/O_3 (3000 ppm O_3) mixture at the temperatures range between 650 and 950 °C for 24 h. The calcined powder was die-pressed and sintered in flowing O_2 at temperatures up to 920 °C, followed by annealing at temperatures between 450 and 550 °C. Thin film was also prepared on the substrates from concentrated solution with controlled viscosity by a dip-coating method.

The specimens were characterized by the X-ray powder diffraction method. DTA-TG analysis was performed at a heating rate of 10 °C min^{-1}. The dc resistivity of the specimens was measured by the four probe method with indium contact electrodes. The magnetization was measured by the vibrating sample magnetometry.

Results and Discussion

Figure 2 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 observed for all the specimens at 200—300 and 400—500°C; the second peak corresponds to thermal decomposition and oxidation of organic groups. In the specimens prepared by the hydrolysis of metal alkoxides, less-noticeable weight loss was observed above 600 °C, while a large weight loss was observed above 800 °C for the specimen prepared without 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 carbonaceous residue from organic groups.

Also, when $Cu(acac)_2$ was used as a starting material insterd of $Cu(OC_2H_4OEt)_2$, more remarkable exothermic peak associated with large weight loss was observed, which corresponds to the thermal decomposition and the oxidation of organic groups. The fact indicates the formation of coordination compounds between $Cu(acac)_2$ and 2-ethoxyethanol, and/or a partially exchange reaction of acac groups of $Cu(acac)_2$ with the solvent.

Figure 3 shows the X-ray powder diffraction patterns of the powders calcined at 850 °C for 12 h, 900 °C for 7 h, and 920 °C for 5 h, followed by the annealing at 450—550 °C in O_2 flow. In the powders prepared by the hydrolysis of metal alkoxides with the

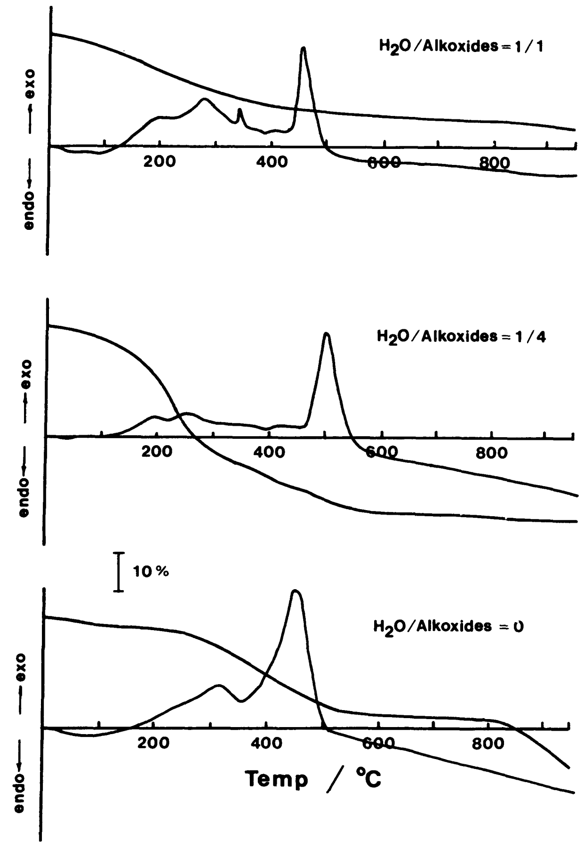

Fig. 2. DTA-TG curves of as-prepared specimens by the hydrolysis of Y-, Ba-, Cu-alkoxides.

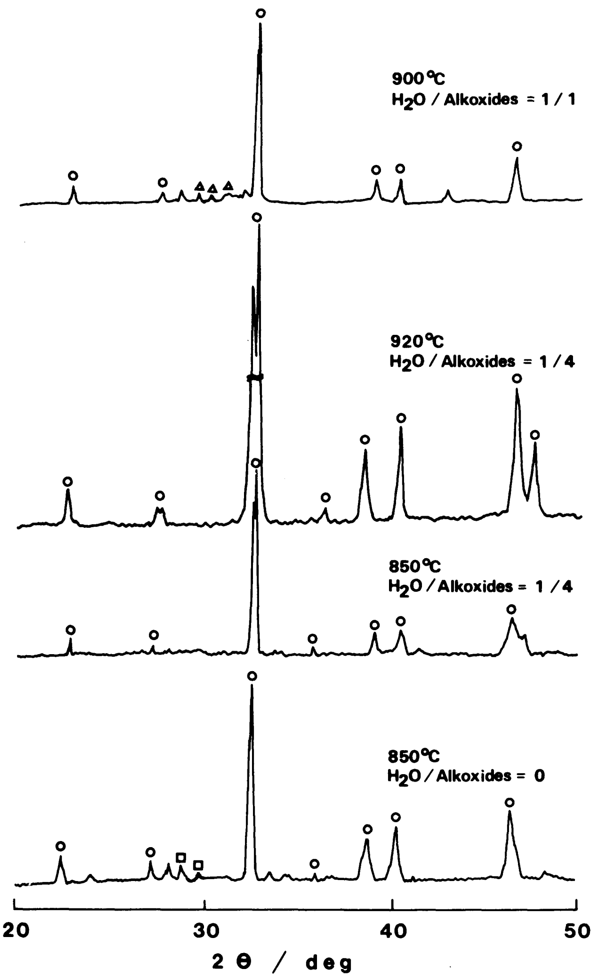

Fig. 3. X-Ray powder diffraction patterns of $Ba_2YCu_3O_{7-\delta}$ powders calcined at 850 °C for 12 h, 900 °C for 7 h and 920 °C for 5 h.
○: $Ba_2YCu_3O_{7-\delta}$ △: Y_2BaCuO_5, □: $BaCuO_2$.

equivalent amount of water, $BaCuO_2$ and Y_2BaCuO_5 were formed together with $Ba_2YCu_3O_{7-\delta}$. On the other hand, chemically homogeneous submicron powders of single phase $Ba_2YCu_3O_{7-\delta}$ were prepared at 850 °C by the controlled partial hydrolysis of metal alkoxides with addition of water less than the equivalent amount.

Figure 4 shows the X-ray powder diffraction patterns of the powders prepared by the calcination of partially hydrolyzed precursors at various temperatures for 12 h. The as-prepared powders were amorphous. $Ba_2YCu_3O_{7-\delta}$ compound formed at 750 °C was of single phase, and its crystallinity was further improved by heat treatment at 850 °C. Furthermore, by flowing O_2/O_3 mixture during the thermal decomposition of organic groups of the precursors, $Ba_2YCu_3O_{7-\delta}$ compound was prepared at the temperature as low as 650 °C. The importance of the utilization of O_3 gas was indicated by suppressed formation of $BaCO_3$. The addition of O_3 results in the direct formation of $Ba_2YCu_3O_{7-\delta}$ compound without any formation of intermediate phases such as $BaCuO_2$ and Y_2BaCuO_5. The carbon content in calcined powders, for example, in pure O_2 flow was 2.24%, which was drastically decreased to 0.94% by flowing O_2/O_3 mixture.

Figure 5 shows the SEM photograph of $Ba_2YCu_3O_{7-\delta}$ powders calcined at 850 °C. The resulting powders were chemically homogeneous, less agglomerated submicron particles, which can be ultrasonically dispersed homogeneously in organic solvents.

Figure 6 shows the dc resistivity of $Ba_2YCu_3O_{7-\delta}$ sintered at 920°C as a function of temperature. The superconducting transition starts at approximately 90 K and the resistance becomes zero at about 83 K. The superconducting-state magnetization, $Ms(H)$, of the fine powders determined by a magnetic balance, is shown at 85 K in Fig. 7. The hysteresis caused by the trap of magnetic flux exists in the $Ms(H)$ curves between the increase and the decrease of the magnetic field (H). The lower critical field H_{c1} was about 0.2 kOe at 85 K and the susceptibility was about −0.016 emu g^{-1}.

Figure 8 shows the fracture surface of the $Ba_2YCu_3O_{7-\delta}$ sintered body. The microstructure consisted of uniform grains of 2—3 μm, and no abnormal grain

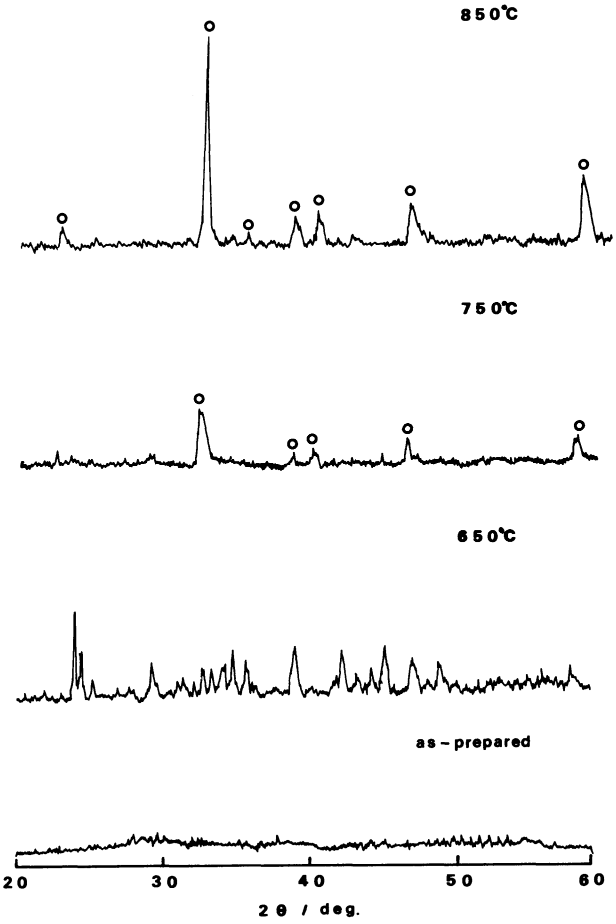

Fig. 4. X-Ray powder diffraction patterns of the powders prepared by the calcination of partially hydrolyzed precursors at various temperatures for 12 h.
O: $Ba_2YCu_3O_{7-\delta}$.

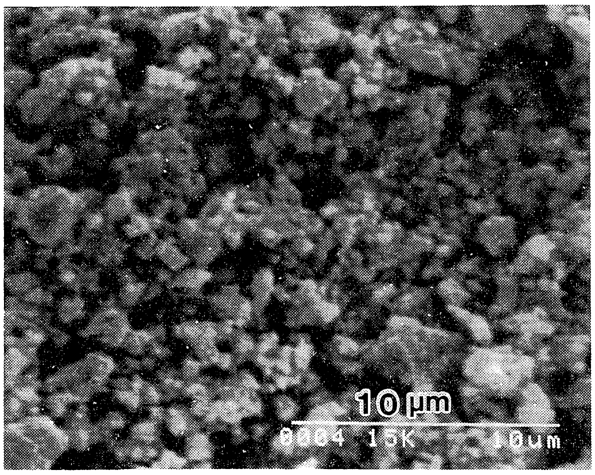

Fig. 5. SEM photograph of $Ba_2YCu_3O_{7-\delta}$ powders calcined at 850 °C.

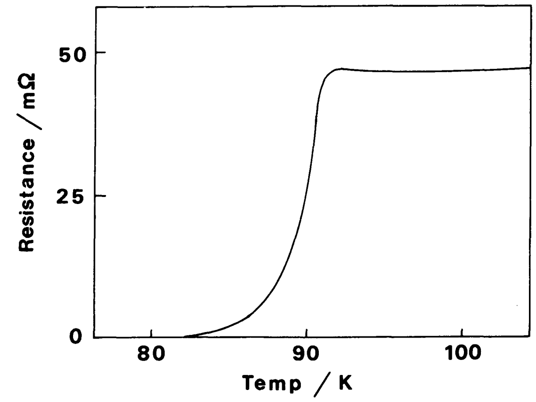

Fig. 6. DC resistivity of $Ba_2YCu_3O_{7-\delta}$ body sintered at 920 °C as a function of temperature.

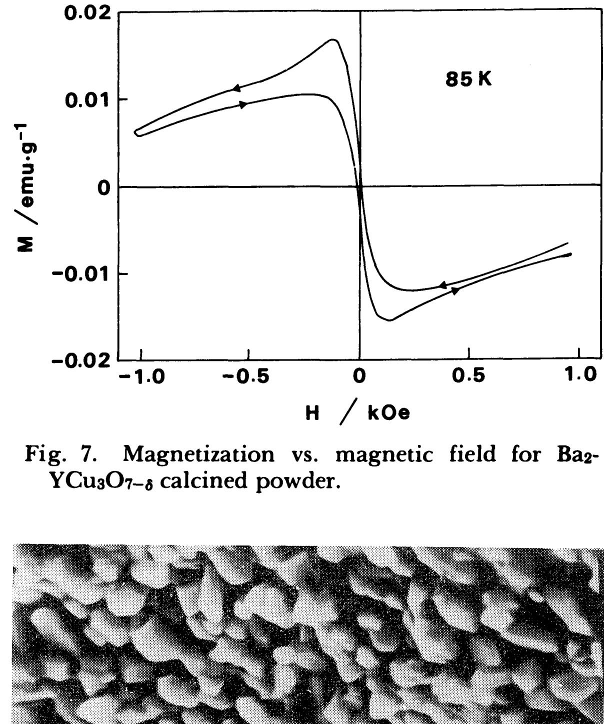

Fig. 7. Magnetization vs. magnetic field for $Ba_2YCu_3O_{7-\delta}$ calcined powder.

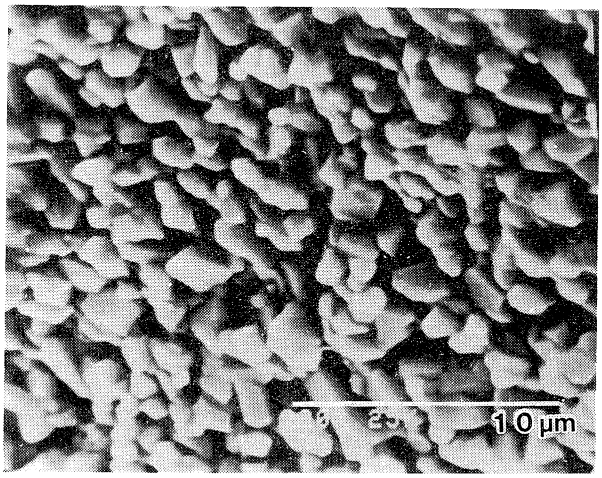

Fig. 8. Fracture surface of the $Ba_2YCu_3O_{7-\delta}$ sintered body.

growth was observed. No significant difference of properties was recognized for the powders or sintered bodies prepared from $Cu(OC_2H_4OEt)_2$ and $Cu(acac)_2$ in a flow of O_2/O_3 mixture.

The further research is in progress to synthesize the epitaxially grown films with c-axis orientation and the fibers of $Ba_2YCu_3O_{7-\delta}$ at lower temperature, on which details will be reported elsewhere.

Conclusion

The synthesis of high-T_c $Ba_2YCu_3O_{7-\delta}$ superconductor in the relatively low temperature range was investigated through organometallic route, using Ba metal, $Y(OPr^i)_3$, and $Cu(OC_2H_4OEt)_2$ or Cu-acetylacetonate as starting materials by use of appropriate solvent.

1) Chemically homogeneous submicron powders of single phase $Ba_2YCu_3O_{7-\delta}$ was successfully prepared at 750 °C by controlled partial hydrolysis of alkoxides.

2) Utilization of O_2/O_3 mixture for the decomposition of the $Ba_2YCu_3O_{7-\delta}$ precursors showed a remarkable effect on suppressing the formation of $BaCO_3$ and lowering the formation temperature of $Ba_2YCu_3O_{7-\delta}$ to 650 °C.

3) It was confirmed by dc resistivity and magnetic susceptibility measurements that the single phase $Ba_2YCu_3O_{7-\delta}$ ceramics thus formed exhibit superconductivity at about 83 K (T_c end).

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