

## Emulsion 건조방법에 의한 고온초전도체 분말제조

엄우식 · 김호기

### Preparation of High Tc Superconductor Powders by Emulsion Drying Method

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**Abstract** The superconducting powders in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and Bi-Pb-Sr-Ca-Cu-O system were easily prepared from water in oil type emulsion by loading each cation into the aqueous phase. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  system, the superconducting orthorhombic phase was formed by calcining at  $750^\circ\text{C}$  for 10h in  $\text{O}_2$ . The size of the superconducting phase powders was submicron. The density of the sintered specimen using this powders was about 95% of the theoretical density and the resistance sharply decreases at about 90K. In Bi-Pb-Sr-Ca-Cu-O system the low Tc phase ( $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_x$ ) was formed by calcining at  $800^\circ\text{C}$  for 10h in a low oxygen partial pressure of 1/20 atm. The shape of calcined powder is thin plate of which size is about  $2\mu\text{m}$  and thickness is smaller than  $0.5\mu\text{m}$ . It was observed that the high Tc phase ( $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ ) was formed by sintering at  $850^\circ\text{C}$  for 30h in oxygen pressure of 1/20 atm without intermediary grinding. The above sintered sample exhibited superconductivity with a  $T_c(\text{zero}) = 105\text{K}$ .

### Introduction

Since the discovery by Bednorz and Muller<sup>1)</sup>, a number of high temperature superconductors based on copper oxide have been discovered. One of the most important results of recent investigations on oxide superconductors is the introduction of the Y-Ba-Cu-O and the Bi-Sr-Ca-Cu-O system<sup>2,3)</sup>. Now it is well known that the superconducting phase of the Y-Ba-Cu-O system is orthorhombic and its composition is  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ <sup>4,5)</sup> and that the Bi-Sr-Ca-Cu-O systems contains a low Tc(80K) phase,  $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_x$ , and a high Tc(110K) phase,  $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ . Takano et al. and subsequently Endo et al. showed that addition of Pb and sintering in low oxygen partial pressure produce a good single high Tc phase sample<sup>6,7)</sup>. These superconductors are usually obtained

via conventional ceramic processing by repeated grinding and firing of the parent oxide. However, this process produces coarse powders and the powders are also contaminated by grinding media. Coprecipitation reactions and sol-gel methods have been reported to overcome these problems<sup>8-12)</sup>. However, these homogeneous precipitation procedures often bring about non-reproducible results and no exact superconducting compositions because the techniques are extremely sensitive to subtle variations in conditions and processing.

We therefore studied an alternate method using an emulsion drying method to produce highly pure and submicron-sized particles with a homogeneous chemical composition.

### 1. Experimental Procedure

To prepare the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  system pow-

ders, the aqueous solution of 0.25 mole was prepared by dissolving  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Y}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  in a distilled water. In Bi-Pb-Sr-Ca-Cu-O system, the best initial composition to obtain the single high  $T_c$  phase ( $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ) is known  $\text{Bi}_{1.84}\text{Pb}_{0.34}\text{Sr}_{1.91}\text{Ca}_{2.03}\text{Cu}_{3.06}\text{O}_y$  as reported by Takano et al.<sup>6)</sup> and Endo et al.<sup>7)</sup> Therefore, we chose this initial composition to prepare aqueous solution. The aqueous solution of 0.07mol was prepared by dissolving  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , in a dilute nitric acid. Emulsifying agent was dissolved into the oil. To make emulsion, aqueous solution was dropped into the emulsifying agent and oil mixture while stirring at room temperature. The kerosene and the tween 85 were used as oil phase and emulsifying agent, respectively. The volume ratio of kerosene, aqueous solution, and emulsifying agent was 70-55/30-20/15-10. Resulting emulsion was water in oil type, meaning that droplets of an aqueous solution are dispersed in an oil phase. After the emulsion was stirred for 6h, it was treated by ultrasonic disruptor for 8min to make aqueous droplets much smaller. Precursor powders were obtained by dropwise addition of the emulsion to a hot kerosene<sup>13)</sup>. During this process, temperature was kept at 180-200°C. We washed the precursor powders with toluene to remove residual oil phase.

The precursor powders were first fired at 400-500°C for 6-10h in air to remove all volatile anions. The calcination was performed at various temperatures for 10h in  $\text{O}_2$  to know lowest temperature at which  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  phase was formed and in oxygen pressure of 1/20 atm to know optimal temperature at which  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  phase was formed for short period of sintering time. Low oxygen partial pressure was controlled with oxygen and nitrogen. The powders were cooled in the

tube furnace in the same atmosphere. Phases were identified by X-ray diffraction with  $\text{Cu-K}\alpha$  radiation and a nickel filter and some powders were examined by scanning electron microscopy. The calcined powders were pressed into pellets without any milling and the pellets were sintered at 850-930°C with increasing sintering time in oxygen and oxygen partial pressure of 1/20 atm without any intermediary grinding. After sintering the pellets were slowly cooled to room temperature in the same atmosphere. The electrical resistances of sintered samples were measured by the four-probe method, and fracture surfaces of the sintered sample were examined by scanning electron microscope.

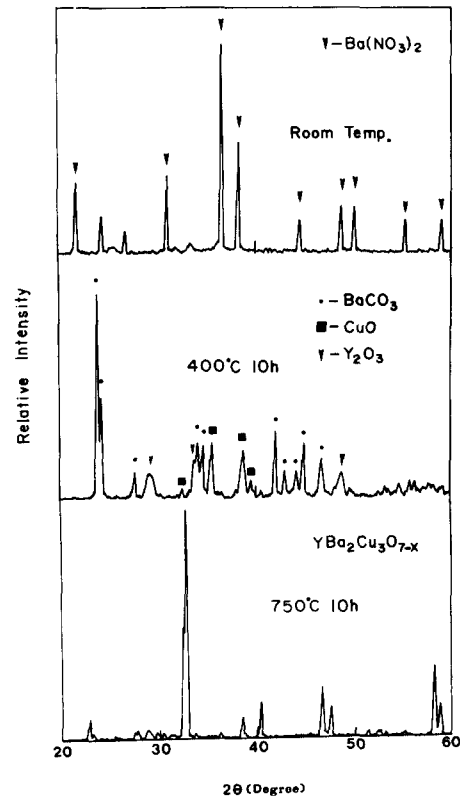


Fig. 1. X-ray diffraction patterns of the Y-Ba-Cu-O system powders calcined at various temperatures in oxygen.

2. Results and Discussion

Figure 1 shows X-ray diffraction patterns of powders dried and calcined at various temperatures in oxygen. From upper pattern, we could know the  $Ba(NO_3)_2$  phase was formed in precursor particles, but couldn't identify the other compound forms of copper and yttrium cations. It is thought that Cu and Y ions exist in an amorphous phase. After heating the precursor powders at  $400^\circ C$ , the cupric oxide, yttrium oxide, and barium carbonate crystallized from the previous phases as shown in Fig. 1 (b). It is clearly seen that crystallization of yttrium oxide, cupric oxide, and barium carbonate takes place before the formation of  $YBa_2Cu_3O_{7-x}$ . The main carbon source to form  $BaCO_3$  may be the emulsifying agent, tween 85, which forms an adsorbed film around the dispersed droplets. Tween 85 (polyoxyethylene sorbitan ester) is able to locate its hydrophilic polyoxyethylene chains in the aqueous phase and allow the lipophilic hydrocarbon chains to escape the oil phase<sup>14,15</sup>. The emulsifying agent may remain during emulsion drying and toluene washing. These phase changes with increasing temperatures are in close agreement with results of other's coprecipitations<sup>8)</sup> and sol-gel synthesis<sup>9)</sup>. From Fig. 1(c), we knew that the lowest calcination temperature to form  $YBa_2Cu_3O_{7-x}$  orthorhombic phase was  $750^\circ C$  in oxygen. This calcination temperature is lower than that of normal process by about  $100^\circ C$ .

Figure 2 shows X-ray diffraction patterns of Bi-Pb-Sr-Ca-Cu-O system powders dried and calcined at various temperatures in air and oxygen pressure of 1/20 atm. From Fig. 2 (a), we could know the  $Sr(NO_3)_2$  phase was formed in the precursor particles, and bismuth, lead, calcium and copper cations exist in an amorphous phase. After heating the precursor powders at  $500^\circ C$ , the calcium carbonate, calcium oxide, cupric oxide, bismuth oxide, and

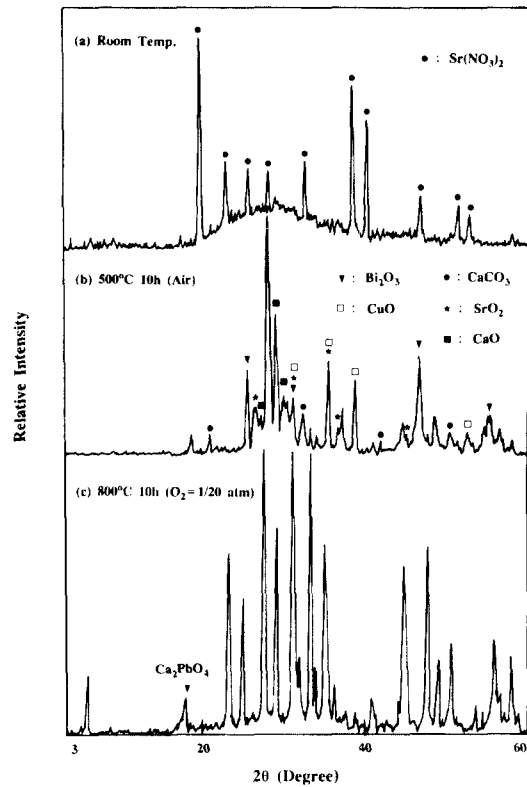


Fig. 2. X-ray diffraction patterns of the Bi-Sr-Ca-Cu-O system powders calcined at various temperature.

strontium oxide crystallized from the previous phases as shown in Fig. 2(b). It is clearly seen that crystallization of these phases takes place before the formation of Bi(Pb)-Sr-Ca-Cu-O superconductor. The main carbon source to form  $CaCO_3$  may also be the emulsifying agent, tween 85. From Fig. 2(c), we knew that  $(Bi, Pb)_2Sr_2Ca_1Cu_2O_x$  phase was formed from calcination at  $800^\circ C$  for 10h in oxygen pressure of 1/20 atm. And  $Ca_2PbO_4$  ( $2\theta = 17.8$ ) was also observed.

SEM photographs are represented in Fig. 3 and 4. Fig. 3(a) and (b) show Y-Ba-Cu-O system powders dried at room temperature and calcined at  $750^\circ C$  for 10h in oxygen. The size of calcined powders is less than  $0.5\mu m$  and the shape is nearly spherical. But the degree of agglomeration is high. Fig. 4(a) shows precursor

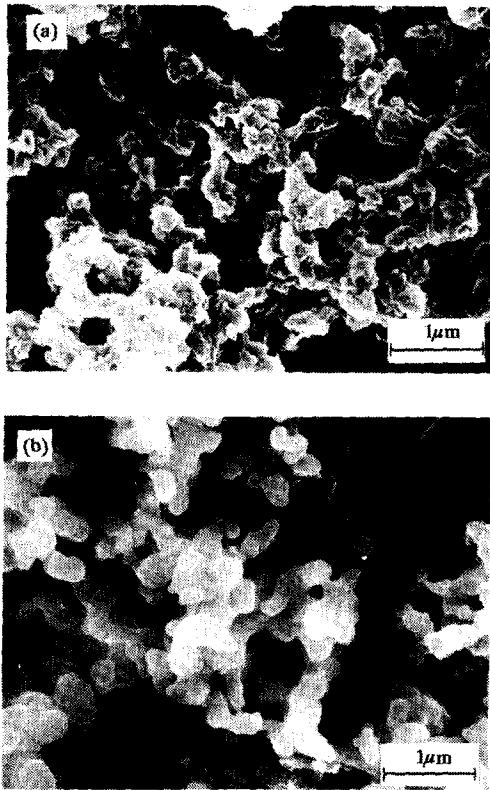


Fig. 3. SEM photographs of the Bi-Sr-Ca-Cu-O system powders (a) dried at room temperature (b) calcined at 750°C for 10h in  $O_2$ .

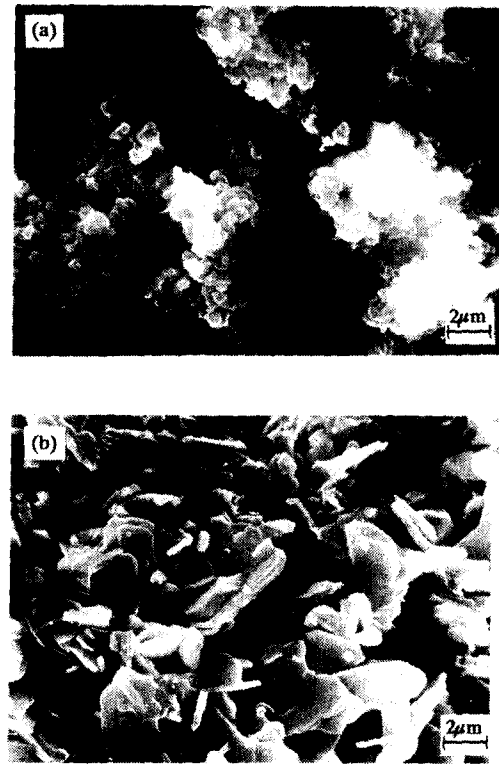


Fig. 4. SEM photographs of the Bi-Sr-Ca-Cu-O system powders (a) dried at room temperature (b) calcined at 800°C for 10h in oxygen pressure of 1/20 atm.

sor powders and Fig. 4(b) shows powders calcined at 800°C for 10h in oxygen partial pressure of 1/20 atm. The shape of powders calcined at 800°C is thin plate of which size about 2 $\mu\text{m}$  and thickness is smaller than 0.5 $\mu\text{m}$ . The phases of calcined powders are  $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$  phase and  $\text{Ca}_2\text{PbO}_4$  as shown in Fig. 2 (c). The plate-like powders are caused by growth direction of plate parallel to the  $c$  plane of the unit cell of  $(\text{Bi, Pb})_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$  phase. We used these calcined powders to prepare sintered samples.

Fig. 5 shows relative densities of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  sample at various sintering temperatures for 12h in oxygen. The densities of the sample increased with increasing sintering temperature from 850°C to 930°C. The relative densities higher than 90% of theoretical value were

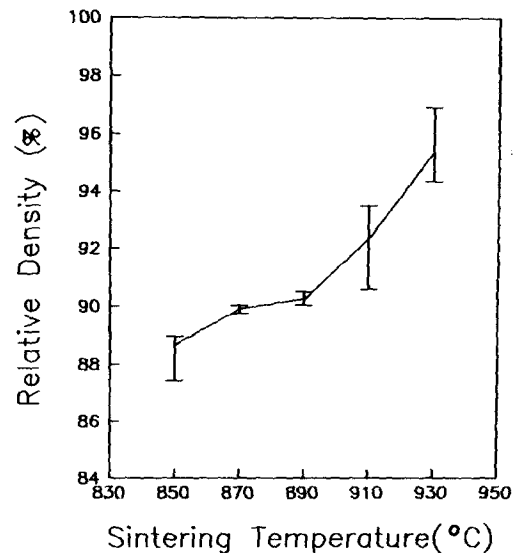


Fig. 5. Relative densities (%) of the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples sintered at various sintering temperatures for 12h in  $O_2$ .

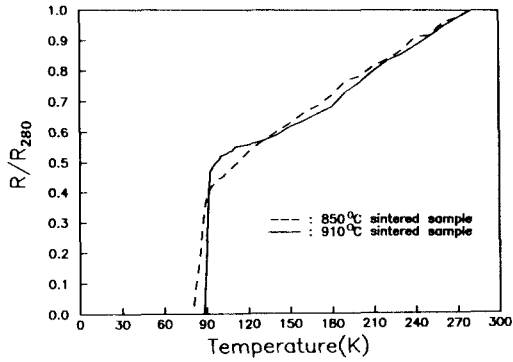


Fig. 6. Resistance-temperature curves for the sintered  $YBa_2Cu_3O_{7-x}$  samples.

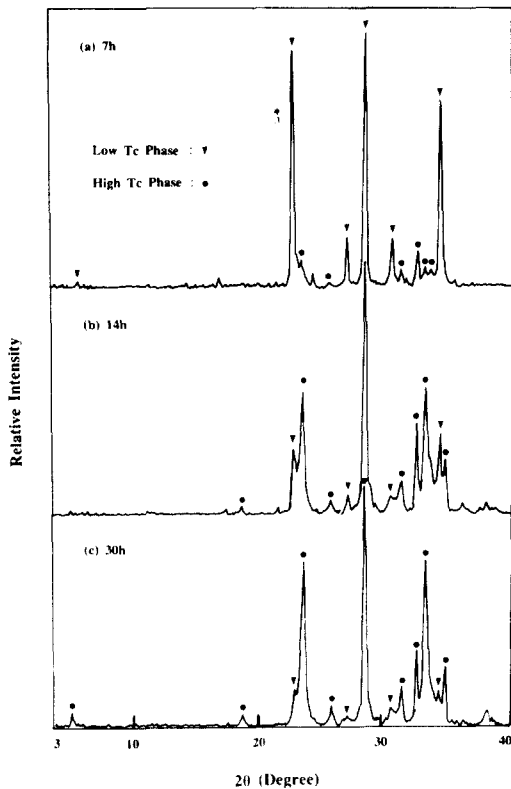


Fig. 7. X-ray diffraction patterns of the Bi-Pb-Sr-Ca-Cu-O samples sintered at  $850^\circ\text{C}$  with increasing sintering time in oxygen pressure of  $1/20$  atm.

observed at samples sintered above  $870^\circ\text{C}$ . The highest average relative density was 95.7% which was the value of the samples sintered at  $930^\circ\text{C}$ . These relative densities are higher than the value of samples prepared by conventional

process. The resistance-temperature curves for sintered samples are shown in Fig. 6. The sample sintered at  $850^\circ\text{C}$  shows superconducting transition temperature is low. But the sample sintered at  $910^\circ\text{C}$  shows the sharp superconducting transition at about 90K.

Fig. 7 shows the X-ray diffraction patterns of the Bi-Pb-Sr-Ca-Cu-O system sample calcined at  $800^\circ\text{C}$  for 10h and sintered at  $800^\circ\text{C}$  for 5h and at  $850^\circ\text{C}$  for several period. The pattern of Fig. 7(a) represents the major phase of the sample sintered at  $850^\circ\text{C}$  for 7h is  $(Bi, Pb)_2Sr_2Ca_1Cu_2O_x$  and a small quantity of  $(Bi, Pb)_2Sr_2Ca_2Cu_3O_x$  phase exists. As shown in Fig. 7(b), as sintering time increase, amount of high Tc phase increases and amount of low Tc phase decreases. The conversion of the low Tc phase to the high Tc phase is almost completed in the specimen sintered for 30h. This sintering period is much shorter than that of normal process and there is no intermediary grinding which is essential to conventional process. In the case of sintered samples using powders calcined at lower or higher temperatures than  $800^\circ\text{C}$ , the sintering time to form high Tc phase was much longer than 80h at  $850^\circ\text{C}$  in oxygen pressure of  $1/20$  atm. From this fact, we knew the calcination temperature around  $800^\circ\text{C}$  is most effective for the formation of high Tc phase is in close agreement with result of other sol-gel method.<sup>11)</sup> The resistance vs. temperature curves for sintered samples are shown in Fig. 8. Zero resistance temperatures increased with increasing sintering time. Resistance sharply drops at about 110K and becomes zero at 105K in the sample sintered for 30h.

### 3. Conclusion

$YBa_2Cu_3O_{7-x}$  and  $(Bi, Pb)_2Sr_2Ca_1Cu_2O_x$  powders could be easily synthesized from the emulsion drying method. In  $YBa_2Cu_3O_{7-x}$ , a pure

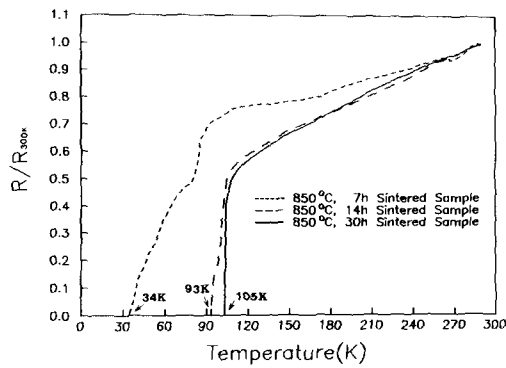


Fig. 8. Resistance-temperature curves for the sintered Bi-Pb-Sr-Ca-Cu-O samples.

orthorhombic phase has been obtained at a temperature as low as 750°C in O<sub>2</sub>. The size of calcined powder was submicron (less than 0.5 μm) and the relative densities of sintered materials were higher than 90% of the theoretical value. These relative densities are higher than the values of samples prepared by conventional process. And the sharp superconducting transition was observed at 90K. In Bi-Pb-Sr-Ca-Cu-O system, the size of calcined powders was small and shape was plate. A single (Bi, Pb)<sub>2</sub>Sr<sub>2</sub>Ca<sub>1</sub>Cu<sub>2</sub>O<sub>v</sub> phase was obtained through sintering at 850°C for 30h in oxygen pressure of 1/20 atm. The sintering time to obtain high T<sub>c</sub> phase is reduced shorter than that of normal process. Sample sintered for 30h shows a zero resistance temperature at 105K.

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