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Direct Preparation of Fine Powders of Bi-Pb-Sr-Ca-Cu-O by Ultrasonic Spray Pyrolysis

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초음파 분무열분해에 의한 Bi-Pb-Sr-Ca-Cu-O의 미분체 제조

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ABSTRACT

Fine powders of the 2212 superconducting phase of bismuth system have been prepared directly from solution using ultrasonic spray pyrolysis. The fine superconducting powders produced by pyrolysis were characterized for the size, shape, and crystalline phase by SEM and XRD. The pyrolysis temperature, flow rate of the carrier gas, residence time of the droplets greatly influenced the size, shape, and crystalline phase. The optimum temperature and flow rate of the carrier gas for the preparation of fine powders of the 2212 superconduting phase were found to be 830℃ and 3 *l*/min, respectively

요 약

초음파 분무열분해법을 이용하여 용액으로부터 1 μm 이하의 크기를 가지는 2212 상의 Bi계 초전도 미분말을 직접 제조하였다. 열분해에 의해 생성된 초전도 미분말의 형상, 크기 및 결정상을 SEM 및 XRD로 확인하였다. 열분해 온도, carrier gas의 유속, 액적의 체류시간은 생성되는 분말의 크기나 형상, 결정상에 큰 영향을 미쳤으며, 2212상의 초전도 미분말을 얻기 위한 최적조건은 열분해 온도가 830℃이고 carrier gas의 유속이 3 *l*/min임을 밝혔다.

1. INTRODUCTION

Since the discovery of the high temperature oxide superconductor by Bednorz and Müller[1], numerous studies have been made on the preparation of the superconducting materials to improve their physical properties as well as to search for new materials.

The oxide superconductors are ceramics and therefore are usually prepared by solid state reaction. By this method, however, it is difficult to achieve homogeneity and to obtain submicron-sized powders. Also the size distribution of the powders is rather wide. On the other hand, it is possible to prepare very fine and homogeneous superconducting powders by starting with a solution containing the constituent elements. So to improve the physical properties of oxide superconductors sol-gel process[2,3], coprecipitation[4,5] and freeze drying[6] have been used. With solution methods in general, one does not directly prepare the superconducting phase. Instead, precursors obtained in the solution processes are pyrolyzed to give oxides which then through solid state reaction yield superconducting powders. During these processes the precursors are subject to contamination and it is difficult to control the size and shape of the powders produced.

In this study we carried out an experiment in which

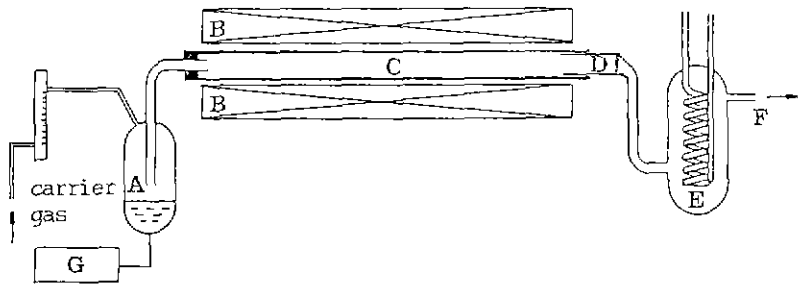


Fig. 1. Schematic diagram of the apparatus.
A. Ultrasonic nebulizer B. Electric furnace C. Quartz tube D. Collector E. Condenser F. Exhaust G. Controller

Bi-Pb-Sr-Ca-Cu-O superconducting powders of submicron size were directly and continuously produced without the precursor stage by combining ultrasonic generation of fine mists of the starting solution and their subsequent pyrolysis. Direct preparation of superconducting powders using ultrasonic spray pyrolysis has been reported for the $YBa_2Cu_3O_{7-\delta}$ system[7,8]. For the Bi-Sr-Ca-Cu-O system Tohge[9] reported on the preparation of the 80 K superconducting powders of the composition Bi:Sr:Ca:Cu=1:1:1:2 without using Pb.

We decided to include Pb which stabilizes the high T_c phase[10] in the preparation of the superconducting powders. The effects of the variations in experimental conditions such as the pyrolysis temperature and the flow rate of the carrier gas on the properties of the powders produced were investigated. The purpose of this study is to prepare fine spherical powders which will subsequently be used to make superconducting thick films by screen printing. It is generally believed that fine spherical particles of uniform size are better suited for screen printing than those of irregular shapes.

2. EXPERIMENTAL

2.1. Starting Materials

The starting solution was prepared by dissolving Bi_2O_3 (5N), $Pb(NO_3)_2$ (3 N), $SrCO_3$ (5N), $CaCO_3$ (3N), and CuO (5N) with nitric acid. The concentration of nitric acid in the final solution was about 0.4 M. The composition was Bi:Pb:Sr:Ca:Cu=1.7:0.5:2:2:3 and the concentration was adjusted to 0.017 M in Bi.

2.2. Preparation of Superconducting Powders and Their Characterization

In Fig. 1 is shown the apparatus for producing superconducting powders. The nebulizer (A) was made by attaching an ultrasonic vibrator (1.6 MHz) to the bottom of a cylindrical vessel. The metal nitrate solution was placed in the nebulizer and then spraying was begun with air as carrier gas. The flow rate of the carrier gas was adjusted between 1 *l*/min and 10 *l*/min. The mists generated were led to a quartz tube (C, 450 mm diameter×900 mm length) enclosed in an electric furnace (B). They were pyrolyzed in the quartz tube and the resulting powders were carried out of the tube and collected by the stainless steel screen (325 mesh) which was placed in the collector (D). The water vapor was condensed at the condenser (E) and the carrier gas was exhausted to a fume hood (F).

The powders thus produced were characterized with XRD (Rigaku DMAX-3B) to identify the crystalline phases, and their sizes and shapes were examined by SEM (Jeol JSM-840A).

3. RESULTS AND DISCUSSION

3.1. Temperature of Pyrolysis

X-ray diffraction data of the powders obtained by setting the flow rate of the carrier gas at 3 *l*/min and varying the pyrolysis temperature between 800℃ and 845℃ are shown in Fig. 2. The pyrolysis zone was 550 mm in length and the residence time of the mists in this region was about 13 s.

For the pyrolysis temperature of 800℃, there appeared peaks for CuO ($2\theta=32.4°$, 38.6°). Ca_2PbO_4 ($2\theta=17.8°$). Ca_2CuO_3 ($2\theta=36.1°$), and the Pb-doped 2201 phase ($2\theta=6.9°$, 25.8°, 29.7°). As the pyrolysis temperature was increased, the peaks corresponding to CuO and Ca_2CuO_3 diminished while that of Ca_2PbO_4 decrea-

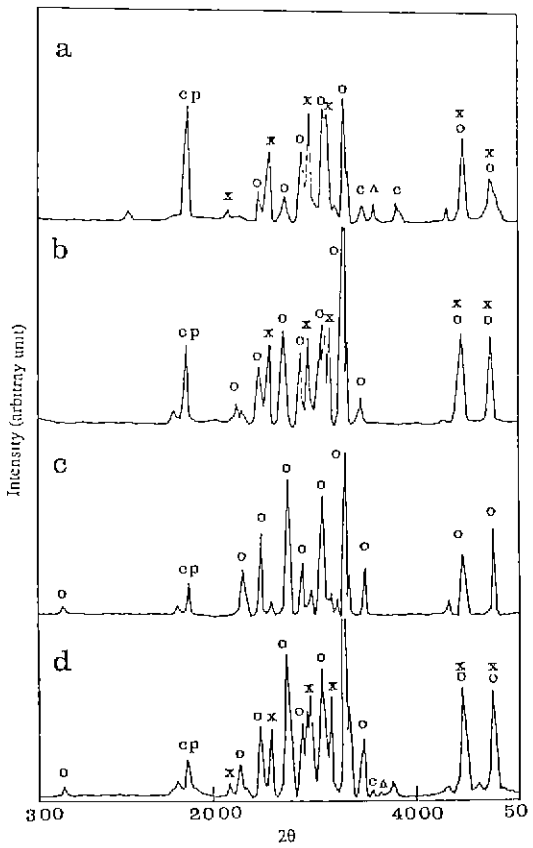


Fig. 2. XRD patterns of the powders obtained at various pyrolysis temperatures.
(a) 800℃ (b) 815℃ (c) 830℃ (d) 845℃ cp: Ca_2PbO_4 c: CuO o: 2212 phase x: 2201 phase Δ: Ca_2CuO_3

sed with concurrent increases in intensities of the peaks due to the Pb-doped 2212 phase (2θ=22.9°, 24.8°, 27.5°). At the even higher pyrolysis temperature of 845℃ the peaks for Ca_2PbO_4 were still small but those for Ca_2CuO_3 and CuO appeared and the 2201 peaks grew up markedly as well.

Since the droplets generated from the nebulizer were rapidly carried into the quartz tube maintained at 800℃ or 815℃, it is thought that the water which is the main constituent of the droplets evaporates and at the same time the nitrates decompose to produce binary or ternary metal oxides. This could be the reason why, except for CuO, oxides such as Bi_2O_3, SrO, and CaO were not detectable with XRD even when the pyrolysis temperature was 800℃.

At 830℃, the 2212 phase was mostly produced indicating that as the pyrolysis temperature increased, the 2201 phase transformed into the 2212 phase and Ca_2PbO_4, CuO, and Ca_2CuO_3 participated in the reaction resulting in the decrease in their concentrations as manifested by the diminution of the corresponding XRD peaks. It was expected that at 845℃ the reaction would further proceed to yield the 2223 superconducting phase, but the 2212 phase decomposed to give the 2201 phase and Ca_2CuO_3.

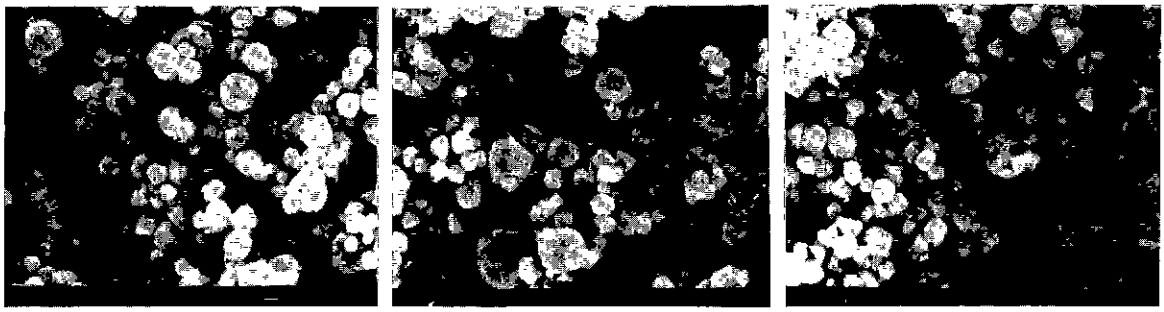
In order for the 2212 phase to transform to the 2223 phase, one mole of reactant is required for each of CaO and CuO. But the result of the decomposition at 830℃ shows no excess Ca_2CuO_3 and CuO. As the temperature is further increased, low melting compound like Ca_2PbO_4 evaporate and are carried away, leaving insufficient amounts of constituents for the generation of the 2223 phase.

In the scanning electron micrographs (Fig. 3) it can be seen that the particles are generally spherical when the pyrolysis temperature is low but become larger and angular with increasing temperature. At 845℃ the angular shape is maintained but the particle size tends to decrese. This result is in accordance with that of Tohge[9] and it is thought that with increasing temperature particle growth, melting, and rapid decomposition of the compounds formed proceed simultaneously.

3.2. Residence Time

The residence time for decomposition can be varied by changing the flow rate of the carrier gas and the length of the pyrolysis zone in the electric furnace. With lower flow rate of the carrier gas, it takes more time for the droplets to decompose and for the powders produced to be carried out of the quartz tube. With longer pyrolysis zone the residence time can be increased at constant flow rate.

In this study the residence time was varied by changing the flow rate, but for comparison, the length of the pyrolysis zone was also changed. The quartz tube was 900 mm long with the inner diameter of 39 mm. The electric furnace consisted of three zones each of which could be temperature controlled independently. The pyrolysis zone lengths were 550 mm and 800 mm. When the pyrolysis zone was 550 mm, the residence times were 39 s, 13 s, and 7 s for the flow rate of 1 l/min, 3 l/min, and 6 l/min, respectively. When



(a) (b) (c)

Fig. 3. Scanning electron micrographs of the powders pyrolyzed at various temperatures. The bars indicate 1 μm (a) 815℃ (b) 830℃ (c) 845℃

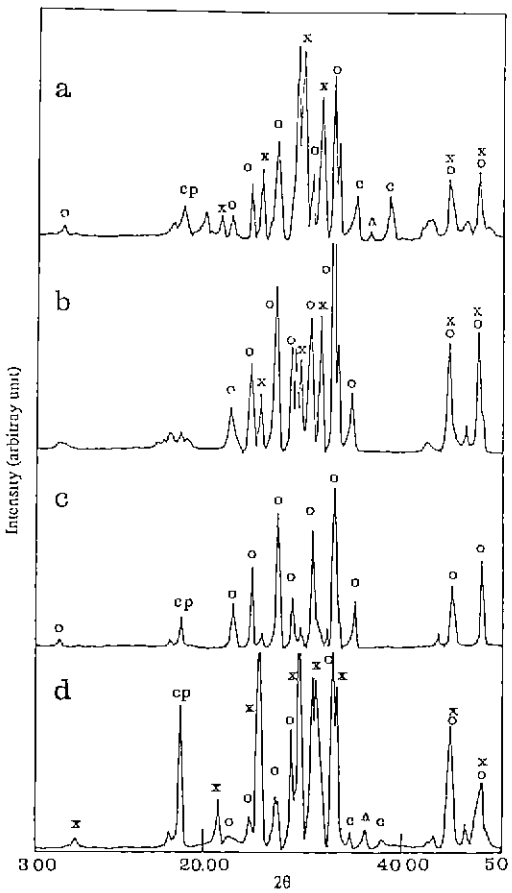


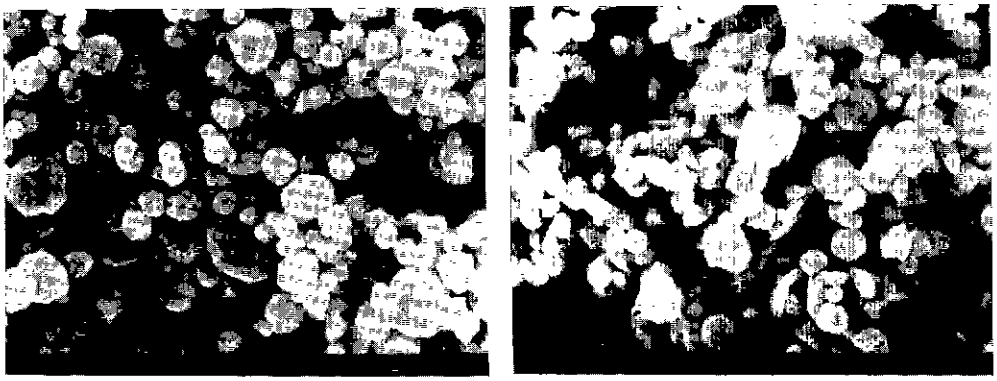
Fig. 4. XRD patterns of the powders pyrolyzed at 830 ℃.
(a) 1 *l*/min 550 mm, 39 s (b) 3 *l*/min, 800 mm, 19 s (c) 3 *l*/mm, 550 mm. 13 s (d) 6 *l*/mm, 550 mm, 7 s cp: Ca_2PbO_4 c: CuO o: 2212 phase x: 2201 phase Δ: Ca_2CuO_3

the pyrolysis zone was 800 mm, the residence time was 19 s for the flow rate of 3 *l*/min.

XRD patterns (Fig. 4) show the appearance of the 2201 phase, Ca_2PbO_4, Ca_2CuO_3, and CuO for the short residence time of 7 s when the pyrolysis temperature was 830℃. Under these conditions the droplets simply do not have enough time for the 2212 phase to be formed before being carried out of the pyrolysis region. This result is similar to that for the lower decomposition temperature of 800℃. On the other hand, when the residence time is increased to about 39 s (flow rate is 1 *l*/min), the XRD peak due to Ca_2PbO_4 is very weak but the peaks for CuO and Ca_2CuO_3 are quite increased compared to the cases where the residence time is short. Therefore in the generation of the 2212 superconducting phase, the flow rate of the carrier gas is as important as the pyrolysis temperature in influencing the formation of the powders. There exists an optimum flow rate and if the rate is higher or lower than the optimum rate then the reaction does not proceed properly or proceeds excessively to cause redecomposition.

As seen in Fig. 5, compared to the flow rate of 3 *l*/min as reference, it is apparent that for the higher flow rate the particles produced are large and spherical, but for the lower flow rate they become smaller and angular. At constant flow rate the reaction progresses more for the lower flow rate and therefore results in decomposition.

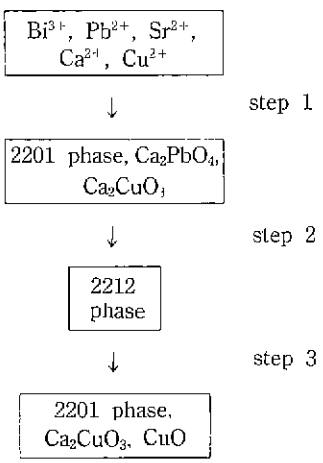
When the length of the pyrolysis zone was varied at the decomposition temperature of 830℃, the longer the pyrolysis zone was, namely the longer the reside-



(a) (b)

Fig. 5. Scanning electron micrographs of the powders pyrolyzed at 830℃. The bars indicate 1 μm. (a) 6 *l*/min (b) 1 *l*/min

nce time was, the more the 2212 phase decomposed. This, as in the case of changing the flow rate, indicates that there is an optimum residence time, considering that the change in the flow rate is equivalent to the change in the residence time during which the droplets are pyrolyzed to yield powders. Above the optmum residence time the 2212 superconducting phase formed decomposes, and below that the reaction does not advance far enough to generate the 2212 superconducting phase. Therefore by spray pyrolysis the following reactions are believed to occur.



step 1: pyrolysis and reaction

step 2: reaction

step 3: decomposition

Since each of the above steps proceeds rapidly, if the pyrolysis temperature is too low or the flow rate is high the droplets decompose to produce powders in step 1. If the pyrolysis temperature is high or the flow rate is low the formation and decomposition occur simultaneously, so the 2201 phase, Ca_2CuO_3, and CuO are thought to be generated.

The 2223 superconducting phase can be expected to form in step 2, but it was not detected in the present study. This might be due to evaporation of elements such as lead and bismuth caused by continuous flow of the carrier gas. It is thus thought necessary to further study the effects of composition and concentration changes and the kinds of carrier gases.

4. CONCLUSIONS

Bi-Pb-Sr-Ca-Cu-O superconducting powders have been prepared by ultrasonic spray pyrolysis of a nitrate solution containing Bi, Pb, Sr, Ca, and Cu.

When using air as a carrier gas the optimum condition for the preparation of the 2212 superconducting powders was obtained with flow rate of 3 *l*/min and pyrolysis temperature of 830℃.

It was found that higher pyrolysis temperature and longer residence time cause the decomposition of the 2212 phase already produced, leading to the formation of the 2201 phase, Ca_2CuO_3 and CuO.

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