

이멀존 건조법에 의해 제조된 Bi(Pb)-Sr-Ca-Cu-O 초전도 분말의 특성 분석

논문
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Characterization of Bi(Pb)-Sr-Ca-Cu-O Superconductor Powder Prepared by Emulsion Drying Method

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국문요약

고순도의 Bi(Pb)-Sr-Ca-Cu-O 초전도 분말을 얻기 위하여 액상법의 하나인 이멀전 건조방법이 응용되었다. 다양한 합성 변수 중 오일과 용액과 계면활성제의 혼합비율을 조정하여 고순도의 Bi(Pb)-Sr-Ca-Cu-O 초전도 분말을 성공적으로 얻을 수 있었다. 이 공정의 최적 혼합비율은 70:20:10 이었다. 관측된 분말은 구형이었으며 마이크론 크기 이하의 균일한 크기를 보였다. 최적의 소결조건 하에 840°C 50시간의 열처리를 통하여 거의 108K를 갖는 초전도 분말이 얻어졌다.

Key Words(중요용어) : Emulsion drying method (이멀전 건조법), Bi(Pb)-Sr-Ca-Cu-O superconducting powder (2223 고온 초전도 분말)

1. Introduction

Since Maeda et al¹⁾ discovered the Bi-Sr-Ca-Cu-O system showing T_c of 110 K, a lot of work have been taken to find the preparation method to obtain the high T_c single phase(2223) in Bi system. It was well known that the formation of high T_c phase(2223) is quite slow and difficult. Conventional solid state reaction process cannot control the physical and chemical properties affected by grain size and the amount of impurities or any other second phases. Especially in solid state reaction the mixing inefficiency and slow decomposition of carbonates in precursors cause the serious disadvantage to get the homogeneous superconducting phase. Nowadays, more emphasis has been placed on the

liquid state processing techniques which can control the morphology, uniform particle size distribution and finally give improved homogeneity of superconductor precursor powders. Therefore various liquid state processing techniques are studied such as coprecipitation²⁾, sol-gel method³⁾, freeze drying method⁴⁻⁵⁾, and emulsion drying method⁶⁾. In co-precipitation method, all the anions in solution are precipitated concurrently, and then powders are separated from solution in the type of precipitation. This method is quite simple, but it is very hard to adjust the chemical stoichiometry of resulting powders due to different precipitate condition and the formation of carbonate by oxalic acid used in this process. Sol-gel method can fabricate ultra-fine size powder. However the formation of carbonate by dissociation of citric acid in solution not only decreases reaction rate but also degrades superconducting properties. Powder preparation via freeze drying method has been attempted to mix the component in atomic scale and to

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prevent the carbonates formation. So far freeze drying method was known as quite useful technique to obtain high $T_c(2223)$ phase in Bi-system within short time. Emulsion drying method utilizes a kinds of colloidal processing and performs by dispersing one of the immiscible liquids in another. The advantages of emulsion drying methods are simple experimental procedure, the easy of compositional control and the fabrication of uniform fine powders. It was firstly applied to fabricate the very pure homogeneous powder in $MgO-Al_2O_3$ system⁷⁾. Emulsifying aqueous salt solution was prepared first and then solvent of oil phase was removed through the routine step; spray drying and kerosene evaporation. Following after oil removal, the powder was obtained by optimum heat treatment. In this paper, we are reporting the preliminary result in terms of powder synthesis of Bi(Pb)-Sr-Ca-Cu-O superconductor by emulsion drying method. Especially the synthesized powder characteristics and superconducting properties derived by emulsion drying method will be systematically investigated and compared with the superconducting powder synthesized by conventional solid state reaction.

2. Experimental Procedure

2-1. Powder Fabrication by emulsion drying method

Overall flow chart for preparation of Bi(Pb)-Sr-Ca-Cu-O system superconductor powders is shown in Fig. 1.

In Bi(Pb)-Sr-Ca-Cu-O system, the best initial composition to obtain the single high T_c phase was known as $Bi_{1.84}Pb_{0.34}Sr_{1.91}Ca_{2.03}Cu_{3.06}O_y$ reported by Endo et al.⁸⁾. First the aqueous solution was prepared by dissolving $Bi(NO_3)_3 \cdot 5H_2O$ in nitric acid, then $Pb(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ in distilled water to 0.1 mol/l solution. The mixing ratio between nitric acid and distilled water was 1 : 5. To make stable emulsion, kerosene and mineral oil was used as oil phase and Alacel 83, Span 60, Span 80, Tween 80, and Tween 85 (ICI

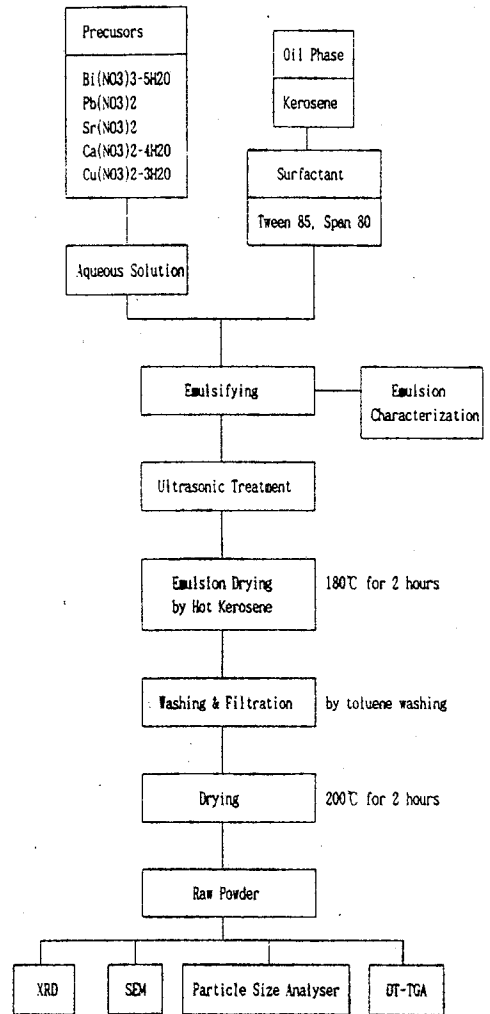
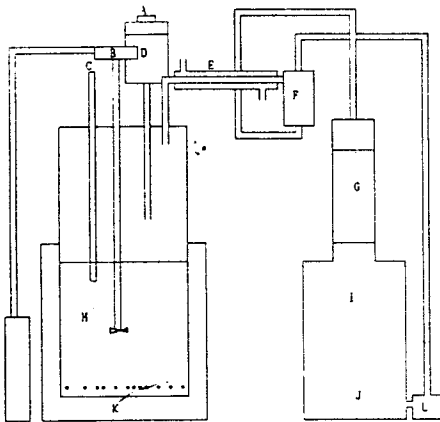


그림 1. Bi-2223상 분말제조 의 이멀존 건조법 개략도

Fig. 1. Schematic diagram of emulsion-drying Bi-2223 phase power preparation

Americas, Inc) which have different HLB (Hydrophilic-lipophilic balance) value was used, as surfactant. Each surfactant was dissolved into the oil phase, and then prepared aqueous solution was dropped into the mixture of oil and surfactant while stirring it under 5,000 rpm for 4h. By varying the volume ratio between kerosene, aqueous solution, and surfactant, the stable emulsion region was formed. The emulsion stability was by systematically observed with

time variation and the aqueous droplet size dispersed in oil phase was examined by optical microscope. Precursor powders were obtained by dropwise addition of the emulsion at the rate of approximately 4-5 ml/min into a hot kerosene bath of which temperature was kept at 180°C within heating mantle. Hot kerosene bath was mechanically stirred by 200 rpm to avoid powders agglomeration. Any gases produced by evaporation of kerosene and other ingredients was designed to circulate through the chamber to react with NaOH solution and thereby remove it. A schematic diagram of designed apparatus is shown in Fig. 2:



- | | |
|--------------------|-----------------------|
| A: Dropping Funnel | B: Mechanical Stirrer |
| C: Thermometer | D: Emulsion |
| E: Cooling System | F: Aspirator |
| G: Glass Bead | H: Hot Kerosene |
| I: NOx Gas Reactor | J: NaOH Solution |
| K: Heating Mantle | L: Magnetic Pump |

그림 2. hot kerosene 건조 장치의 개략도
 Fig. 2. Schematic diagram of hot kerosene drying apparatus

After bath was cooled to room temperature, the precursor powder was washed several times with toluene to remove the residual oil phase. Then the powder was dried at 100°C for 24h.

2-2. The characteristics of precursor powders and heat treatment condition.

The morphology, particle size, and agglomerated state of obtained precursor powders were examined using SEM, differential thermal analysis(DTA), and thermogravimetric analysis (TGA) for thermal properties and heat treatment conditions of the precursor powders. Precursor powders were first fired at 500°C for 5h, then calcined 730°C-810 °C with 20°C intervals to find out optimum calcination conditions by examining XRD pattern of calcined powders. The calcined powder were ground and pressed into the form of a pellet 1cm in diameter under pressing of 500kg/cm². The pellet was sintered at various temperature under oxygen partial pressure of 1/13 atm. to determine the optimum sintering condition. Also, superconducting properties were examined by X-ray diffraction patterns as increasing heat treatment time, 12, 24, 48, 72, and 100h. The transition temperature to the superconducting state were determined from the sintering temperature dependence of the electrical resistance using standard four-probe method and AC susceptibility was measured as sintering time increased under 10 gauss magnetic field.

3. Results and Discussion

3-1. Powder Characteristics.

Using various surfactants, we could establish the stable emulsion preparation condition which maintained the emulsion stability above 24h.

In the preliminary experiments, we obtained very stable emulsion after the mixing of kerosene as oil phase and Span 80 or Tween 85, and aqueous solution. This synthesis condition was kerosene : aqueous solution : surfactant = 70 : 20 : 10. The optical microscopic measurement of each droplet size is shown in Fig.3.

The emulsion using Tween 85 was uniform spherical particles of about 3-4 μm, whereas the emulsion using Span 80 was uniform particle size but the recovery of uniform particle size powders was expected to difficult due to the serious

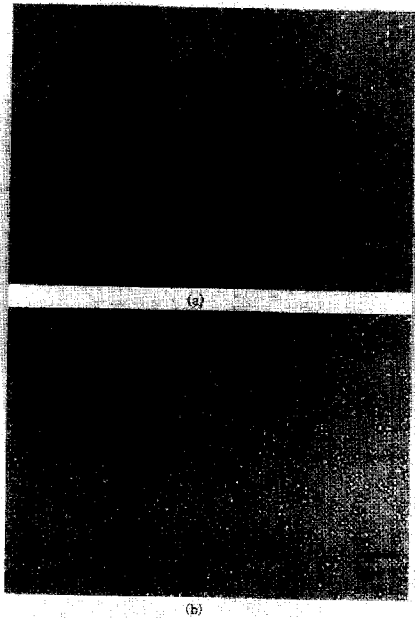


그림 3. W/O type 이멀존의 광학상
 (a) Tween 85 사용시 (b) Span 80 사용시
Fig. 3. Optical photographs of W/O type emulsion prepared by
 (a) using the Tween 85
 (b) using Span 80

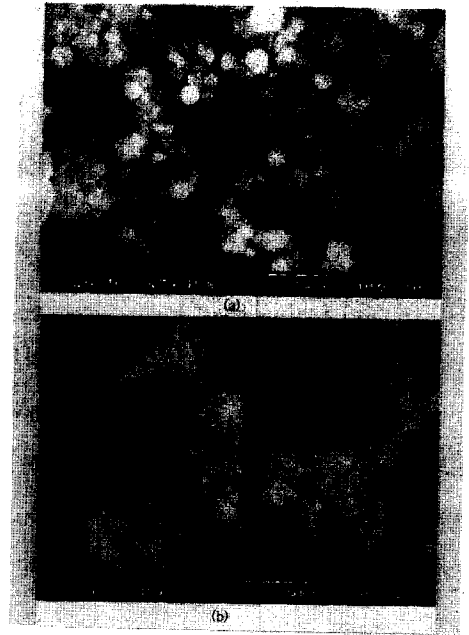


그림 4. 상온에서 건조된 Bi(Pb)SrCaCuO의 SEM 상(a) Tween85 (b) Span 80
Fig. 4. SEM photographs of the Bi(Pb)SrCaCuO powders dried at room temperature using
 (a) Tween85 (b) Span 80

agglomeration of the droplets. Generally, the type of emulsion which tend to form depend on the HLB value of surfactant used in emulsion synthesis, in this experiment W/O(water-in-oil) type emulsion was produced regardless of surfactant type but Tween 85 produced more stable W/O type emulsion than others. SEM measurements of precursor powders were shown in Fig 4.

In Tween 85 surfactant, spherical powders under 1 μm were obtained; however in Span 80 the spherical powders were agglomerated state as good as emulsion droplet observation results. Compared droplet size of emulsion with the dried powders, the latter was more fine, because particles became smaller due to shrinkage and cracking during drying process. As a result, we used emulsion powders derived from Tween 85 surfactant hereafter. Fig 5 shows DTA-TGA

results of precursor powders.

The peak of DTA at about 270°C represents the reaction caused by organic materials such as residual kerosene, surfactant, and another several peaks are observed before reaching melting temperature at 870°C. Exothermic peak at 400°C is expected as the reaction to 2201 phase formation, the peaks at 625°C and 710°C result from the decomposition of nitrate salts, and at about 780°C and 810°C from the reaction to 2212 phase formation. These results were, also, observed in TGA showing weight loss. The decrease of TGA line at 270°C about 30% weight loss results from evaporative combustion of organics adhered to precursor powders physically and chemically.

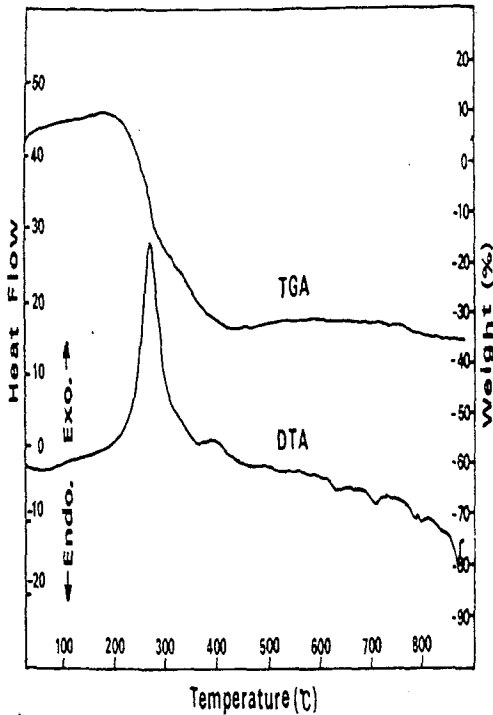


그림 5. Tween85 계면활성제를 사용하여 상온에서 건조된 Bi(Pb)SrCaCuO의 DTA와 TGA결과

Fig. 5. Results of DTA and TGA for Bi(Pb)SrCaCuO powders dried at room temperature using Tween85 surfactant

3-2. Heat Treatment Characterization

Fig. 6 shows the X-ray diffraction pattern of the sample calcined at various temperatures for 24h after drying at 500°C for 5h.

We confirm Ca_2PbO_4 as well as low- T_c 2201 phase at about 730°C.

The conversion of 2201 phase to 2212 phase increases as the sintering temperature increases, and stable 2212 phase was formed at 810°C. From these facts, we decided the calcination temperature around 810°C for 24h in air was the most effective condition for our experiment. After making the calcined powders into pellets, to decide the optimum sintering condition, oxygen partial pressure was varied at various temperatures in argon atmosphere and obtained

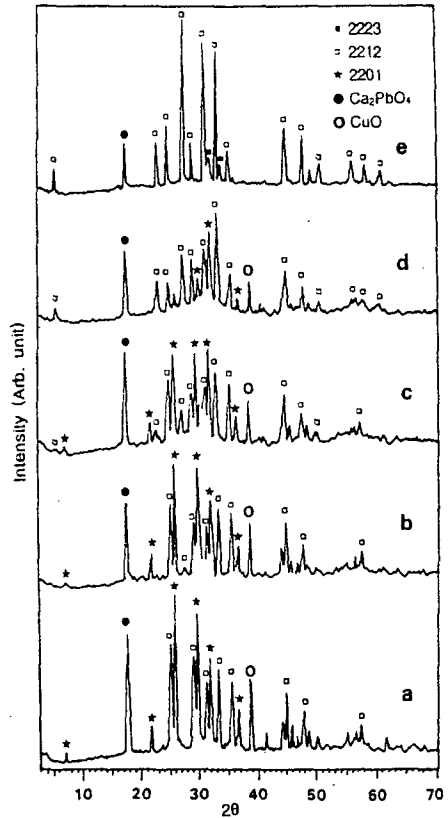


그림 6. 대기중에서 24시간동안 다양한 온도로 하소한 Bi(Pb)SrCaCuO 분말의 XRD 패턴 (a) 730°C (b) 750°C (c) 770°C (d) 790°C (e)810°C

Fig. 6. X-ray diffraction patterns of the Bi(Pb)SrCaCuO powders calcined at various temperatures for 24 hours in air (a) 730°C (b) 750°C (c) 770°C (d) 790°C (e) 810°C

optimum result was sintering at 840°C in argon atmosphere of 1/13 oxygen partial pressure. Fig 7 shows the X-ray diffraction pattern of the sample sintered at above condition for various times.

The 2223 phase was the main phase regardless of sintering time, and as sintering time increased the amounts of 2212 phase was decreased and in the end, 2223 phase was completely obtained in the specimen sintered for over 48h. It was well known fact that in the case of solid-state

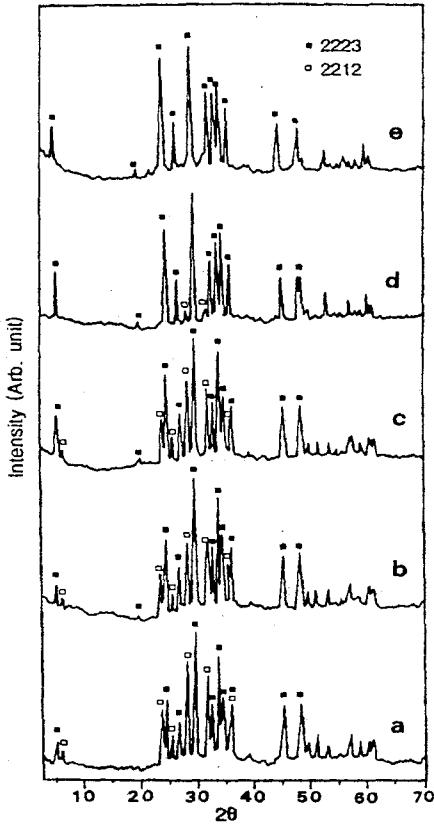


그림 7. 1/13 산소분위기로 840°C에서 다양한 유지시간동안 소결된 Bi(Pb)SrCaCuO 시편의 XRD 패턴 (a) 12 hrs. (b) 24 hrs. (c) 48 hrs. (d) 72 hrs. (e) 100 hrs.

Fig. 7. X-ray diffraction patterns for sintered Bi(Pb)SrCaCuO specimen with various holding time at 840°C in 1/13 oxygen atmosphere (a) 12 hrs. (b) 24 hrs. (c) 48 hrs. (d) 72 hrs. (e) 100 hrs.

synthesis powder samples, the sintering time to form high T_c phase was much longer than 150h at 840°C. Using the equation of $I_{h(0010)} / (I_{h(0010)} + I_{l(008)})$ (I_h : 2223 phase, I_l : 2212 phase), we could obtained the high T_c phase of about 98% was obtained in the sample sintered at 840°C for 72h. The result of this is in close agreement with the result of Fig 8 for critical temperature measurement at various temperatures.

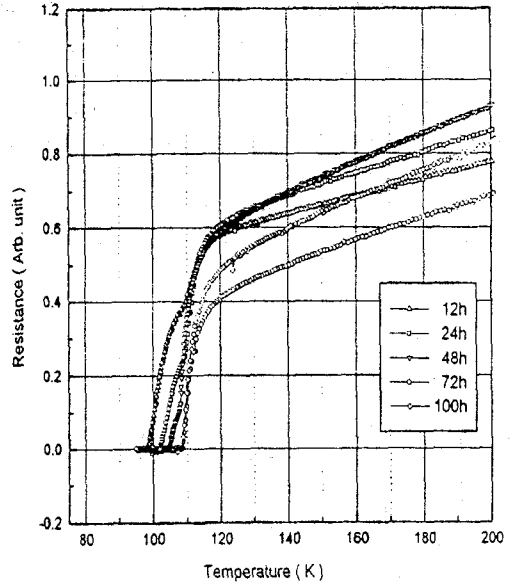


그림 8. 840°C에서 시편의 1/13 산소분위기에서 시간이 증가할때의 저항-온도 곡선

Fig. 8. Resistance-temperature curves for sintered specimen at 840°C with increasing time in 1/13 oxygen atmosphere

For the samples sintered for 12h, 24h, and 48h the tail portion of the critical temperature curves become shortened and critical temperature increased and for 72h and 100h zero resistance of 108K without tail was obtained. Thus we could fabricate high T_c phase with more shorten time than conventional solid-state synthesis samples. But, we cannot decide the 2212 phase and 2223 phase distribution by only critical temperature measurement as shown in Fig 8. It was reported that the critical temperature of high T_c phase was measured in the sample with a relative amounts of 2212 low T_c phase. For verification Fig 9 shows AC susceptibility curves of the samples sintered at 840°C for 48h and 100h under 10 gauss magnetic field applied parallel to the c-axis of the samples.

Magnetization curves show abrupt decrease at about 108K indicating the formation of superconducting properties by Meissner effect but slow decrease at about 80K indicating the

existence of residual low T_c phase in the sample. Under the critical temperature of high T_c phase in Fig 9 relatively wide transition width indicates the presence of the 2212 low T_c phase and impurity phase, which identified by X-ray diffraction patterns. More work to be performed in order to found the optimum fabrication condition for the complete high T_c phase formation.

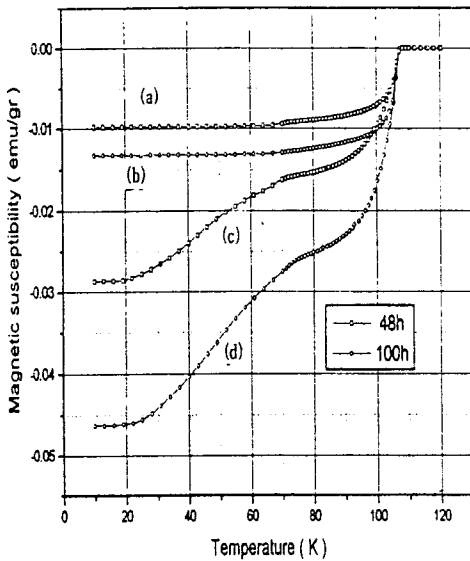


그림 9. 840°C 1/13 산소분위기에서 다양한 유지 시간으로 소결한 시편의 자화율-온도곡선 ((a) 와 (b): 전기장을 가하지 않고 냉각한 경우, (c) 와 (d): 전기장을 가하고 냉각한 경우)

Fig. 9. Magnetic susceptibility-temperature curves for sintered specimen with various holding time at 840°C 1/13 oxygen atmosphere ((a) and (b): zero field cooling, (c) and (d): field cooling)

4. Conclusion

We could fabricate Bi(Pb)-Sr-Ca-Cu-O system superconductor powders with high T_c phase via emulsion drying method. The overall optimum conditions for the stable emulsion synthesis were established. The obtained emulsion powders were the spherical particles of under 1μm showed narrow particle size distribution. The high T_c phase was obtained by heat treatment the emulsion driven powders at 840°C under oxygen partial pressure of 1/13 atm. for above 50h.

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