The Journal of the Korean Institute of Electrical and Electronic Material Engineers. Vol. 9, No. 7, pp.680-689,1996.

SrCaCuO와 BiPbCuO 이중층의 상호 확산에 의해 제조된 Bi(Pb)SrCaCuO 초전도체

논 문 9-7-5

Bi(Pb)SrCaCuO superconductor fabricated by interdiffusion of SrCaCuO and BiPbCuO double layers

최효상*, 이중근*, 정동철**, 한병성**
(Hyo-Sang Choi, Jung-Kun Lee, Dong-Chul Jung, Byoung Sung Han)

요 약

SrCaCuO와 BiPbCuO 화합물로 이루어진 이중층시료가 만들어 졌으며, 소결과정에서 나타나는 확산과 입자간의 상호작용으로 108K의 임계온도를 나타내었다. 이 시료는 820℃에서 0 - 210 시간동안 소결되었다. 초전도체의 생성, 성장메카니즘과 임계온도의 관계가 연구되었으며, 최적조건은 820℃에서 210시간 소결하고 SrCaCuO와 BiPbCuO의 도포비가 1 : 0.6인 시편에서 나타났다. 또한 이중층시료에서 가장 좋은 조성비는 $Sr_2Ca_2Cu_2O_x$와 $Bi_{1.9}Pb_{0.5}Cu_3O_y$ 이었다.

Key Words(중요용어) : double layer(이중층), growth mechanism(성장메카니즘), spread volume ratio(도포비), composition(조성)

1. Introduction

The discovery of the LaBaCuO superconductor by Bednorz and Müller in 1986 has lead to the appearance of $YBa_2Cu_3O_x$ showing superconductivity above 77 K.[1)] Research in high critical temperature superconducting material having higher critical temperature has been undertaken.[2-4)] The subsequent achievement has created enormous activity within the scientific community. So far, one of the greatest contributions has come from the BiSrCaCuO superconductor which substitutes Ca for a part of Sr in BiSrCuO without rare-earth element. This BiSrCaCuO superconductor is cheap and water-resistant in comparison with YBaCuO superconductor. Unfortunately, considering the application in 77 K, the problem is thermal stability in this system having a critical temperature of 80 K(low Tc phase). Thus, the concern has been concentrated on the fabrication of a high Tc superconductor above 110 K(high Tc phase).[5 6)]

In order to increase volume % of the high Tc phase in BSCCO, Ca and Cu heat treatment in an oxygen atmosphere, Pb doping, and sintering of long time periods for the formation of the phase have been studied. In a report by M. Takano et al.,[7)] the Pb-doped specimen having Tc of 108 K was stabilized, substituting a small amount of Pb for Bi and sintering for a long time. Sintering for 200 hours are needed for stabilization of Pb-doped superconducting samples.[8 9)] Until recently, the growth mechanism of the high temperature superconducting phase was not known certainly.

A superconductor using diffusion mechanism of double-layer pellet containing $Sr_2Ca_1Cu_2O_x$ and $Bi_2Pb_{0.3}Cu_2O_y$ was fabricated in a method different from the solid reaction method. Thus, the main object of the current work was to

* : 한전 전력연구원,
** : 전북대학교 전기공학과
접수일자 : 1995년 3월 28일
심사완료 : 1996년 4월 6일

examine systematically the microstructural phase generation process of the BiPbSrCaCuO system under a carefully controlled diffusion process. It was our intention that optimum composition and the basis for process and the sequential results.

2. Experimental procedure

The specimens were fabricated from the diffusion reaction of the samples of A(SrCaCuO) and B(BiPbCuO) in these experiments. The A specimen was calcined at 760 ℃ for 6 h in an air atmosphere, crushed into powder and recalcined at 820 ℃ for 12 h. The B specimen, being used to the formation of spread volume or pellet layer, was calcined at 400 ℃ for 6 h in an air atmosphere, crushed into powder and recalcined at 630 ℃ for 12 h. In succession, the samples were grinded into very fine powder in the mortar and sieved by mesh #170. These were immediately pressed into disc pellets with a diameter of 10 mm and a thickness of 2 mm. Parts of B samples were grinded in form of powder with a very small size in order to spread on A samples.

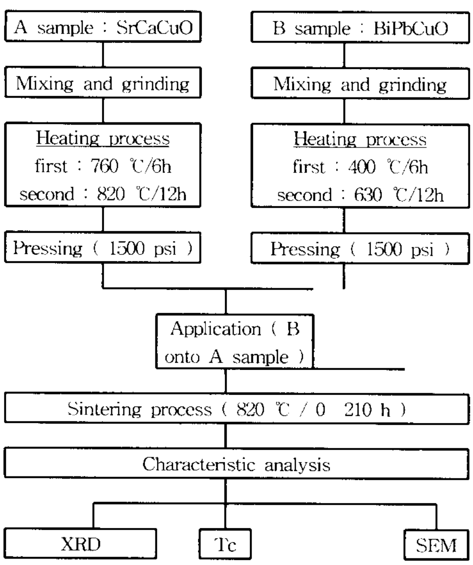


그림 1. 시편제작 과정

Fig. 1. Block diagram for sample preparation

[Experiment 1]

In order to find out optimum condition, Samples were painted with spread volume ratio of 1 : 0.2, 1 : 0.4, 1 : 0.6 respectively (composition : A($Sr_2Ca_2Cu_2O_x$) b($Bi_{1.9}Pb_{0.5}Cu_3O_y$))

[Experiment 2]

In order to find out optimum sintering time, specimens having optimum spread volume 1 : 0.6 in experiment 1 were heated at 820 ℃ for 24 h, 120 h, 210 h respectively (composition : A ($Sr_2Ca_2Cu_2O_x$) b ($Bi_{1.9}Pb_{0.5}Cu_3O_y$)). And then, double-layer pellets pressed at 1500 psi were made by amassing the B pellets onto the A pellets. The samples prepared with the disc pellets were sintered at 820 ℃for 0 - 210 hours in a low oxygen pressure. After sintering, these were cooled down in the furnace. Following also were experiments for the examination of the growth process due to diffusion and optimum conditions for the Bi-based superconducting growth.

[Experiment 3]

In order to find out optimum composition of A and B samples, experiment having compositions of the following table 1 was carried out based on experiment 1, 2 (spread volume 1 : 0.6, sintering temperature 820 ℃, sintering time 210 h)

표 1. A와 B 시편의 조성비

Table 1. Composition of A and B samples.

Sr-Ca-Cu	Bi-Pb-Cu	critical temperature
2-2-1	1.9-0.5-3	0 K
2-2-2	1.5-0.5-3	100 K
2-2-2	1.9-0.5-3	108 K (optimum)
2-2-3	1.5-0.5-3	100 K
2-2-3	1.9-0.5-3	70 K

[Experiment 4]

In order to consider the effects dependent upon the sintering of experiment 3 optimum composition, we observed the characteristics of the sintering time and each stage of the sintering process as shown in table 2.

표 2. 소결처리의 각 단계에서 얻은 시편

Table 2. Sample taken at each stage of sintering process.

sample	temperature(℃)	sintering time(h)	note
1	25	0	pellet
2	760	4 ℃/min.	rising stage
3	820	"	sintering process
4	"	1	"
5	"	50	"
6	"	210	"

3. Results and discussions

3-1. The measurement of the electrical resistance

Fig. 2 shows the results of critical temperature based on experiment 1 When the spread volume ratio was 1 : 0.6 (Fig. 2c), the critical temperature of the specimen had the highest value and it is 70 K. Fig. 3 shows the results of critical temperature based on experiment 2. Although the samples have little change with sintering time, that of 210 hours (Fig. 3c) represented the highest Tc.

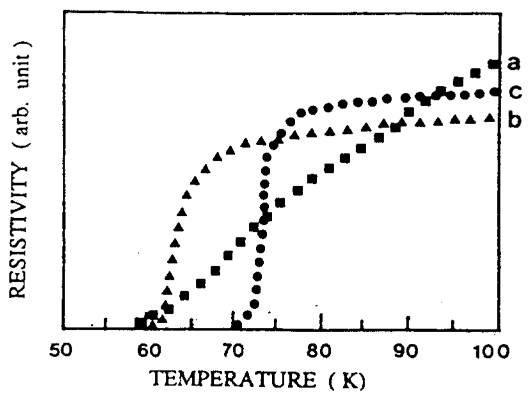


그림 2. 820 ℃에서 210시간 소결한 BiPbSrCaCuO계 초전도체의 도포비에 따른 임계전이온도

Fig. 2. Resistivity vs temperature plot with spread volume ratio (A:B) of BiPbSrCaCuO superconducting system sintered at 820 ℃ for 210 h. (a) 1 : 0.2 (b) 1 : 0.4 (c) 1 : 0.6

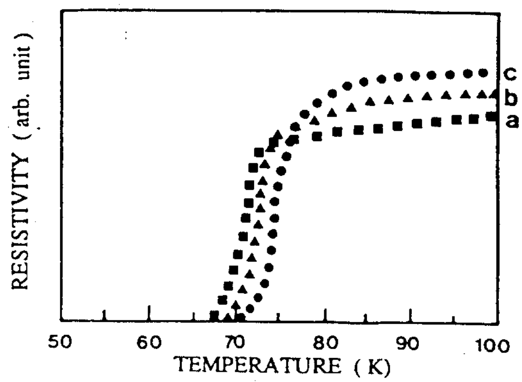


그림 3. 도포비 1 : 0.6, 소결시간 820 ℃인 BiPbSrCaCuO계 초전도체의 소결시간에 따른 임계전이온도

Fig. 3. Resistivity vs temperature plot with sintering time of BiPbSrCaCuO super-conducting system (spread volume ratio ; 1:0.6, sintering time : 820 ℃) (a) 24 h. (b) 120 h. (c) 210 h.

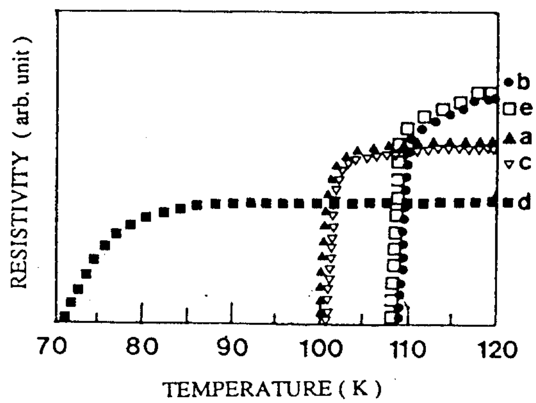


그림 4. A, B 시료의 조성비에 따른 임계전이온도 (소결시간 : 820℃, 도포비 1 : 0.6, 소결시간 210 h)

Fig. 4. Resistivity vs temperature plot of A,B composition with a ratio of A/B sample (sintering temperature : 820 ℃, spread volume ratio ; 1:0.6, sintering time : 210 h.) (a) A : $Sr_2Ca_2Cu_2O_x$, B : $Bi_{1.5}Pb_{0.5}Cu_3O_y$ (b) A : $Sr_2Ca_2Cu_2O_x$, B : $Bi_{1.9}Pb_{0.5}Cu_3O_y$ (c) A : $Sr_2Ca_2Cu_3O_x$, B : $Bi_{1.5}Pb_{0.5}Cu_3O_y$ (d) A : $Sr_2Ca_2Cu_3O_x$, B : $Bi_{1.9}Pb_{0.5}Cu_3O_y$ (e) $(Bi,Pb)_2Sr_2Ca_2Cu_3O_x$ prepared by solid state reaction

Fig. 4. shows electrical resistance measured at the condition of the various composition (Fig. 4-a ~ 4-e) with spread volume 1 : 0.6 and sintering time 210 h. In Fig. 4-b, we see that the results correspond with those of Fig. 4-e having the critical temperature 108 K of the solid state reaction method.[11-13] Based on the X-ray diffraction pattern of Fig. 7-e, high critical temperature was obtained due to the increase of high Tc phases and decrease of low Tc phases according to a long sintering process. Also, the critical temperature of Fig. 4-c, 4-d had low value against the others. It was believed that the composition rate did not fit.

3-2. X-ray diffraction patterns

Fig. 5 shows an X-ray diffraction patterns for the specimen having different spread volume ratio and sintered at 820 ℃ for 210 h. The low Tc phase (2212), CuO and Bi_2CuO_4 phase were observed at the samples of $Bi_2Pb_{0.3}Cu_2O_y$ in upper layer, and the low Tc phase (2212), CuO and $CaPbO_3$ phase at $Sr_2Ca_1Cu_2O_x$ in lower layer. We found that the sample of spread volume ratio of 1 : 0.6 (Fig. 5.c) had the higher intensity than that of spread volume ratio of 1 : 0.2 (Fig. 5.a). It was believed that the mixtures of Bi and Pb melted throughout sintering process at 820 ℃ diffused through grains. Fig. 6 shows an X-ray diffraction patterns for the specimen having different sintering time with spread volume ratio 1 : 0.6 at 820 ℃. In upper layer sample of $Bi_2Pb_{0.3}Cu_2O_y$, the low Tc phase decreased by increase of sintering time and CuO phase increased. It is believed that low Tc phase in the beginning of sintering was grown from upper layer to lower layer with a long sintering time. Also, CuO phase was little grown from upper layer to lower layer.

An X-ray diffraction pattern was used to obtain superconducting property for the sintered specimen in the proper condition (sintering temperature : 820 ℃, spread volume ratio 1 : 0.6, sintering time 210 h, composition A : $Sr_2Ca_2Cu_2O_x$, B : $Bi_{1.9}Pb_{0.5}Cu_3O_y$) (Fig. 7). Before sintering, many mixed phases were observed (Fig.7a) As the temperature was increased, the

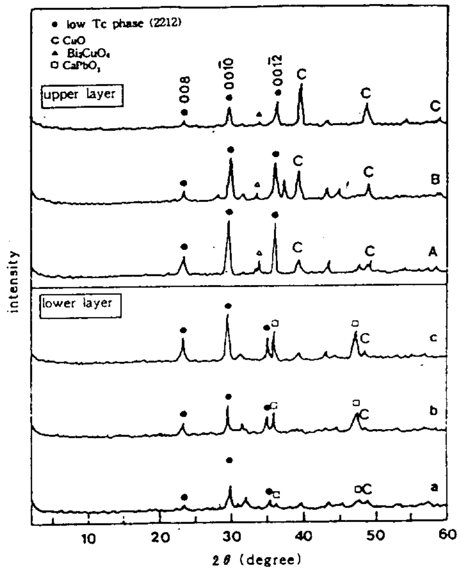


그림 5. 820 ℃에서 210시간 소결한 BiPbSrCaCuO계 초전도체의 도포비에 따른 X선 회절패턴

Fig. 5. X-ray diffraction patterns of BiPbSrCa-CuO superconducting system of varing spread volume ratios (A:B), sintered at 820 ℃ for 210 h.

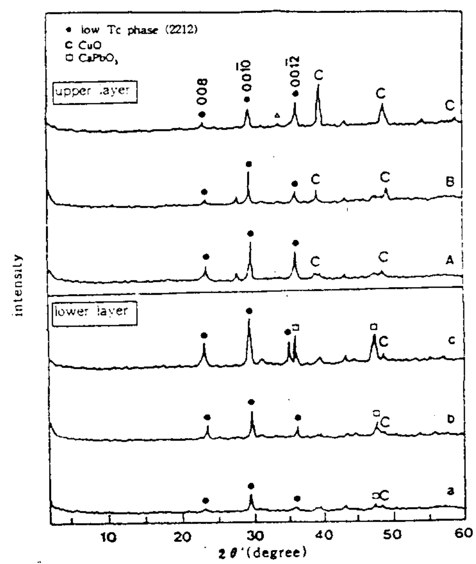


그림 6. 도포비 1 : 0.6에서 소결시간에 따른 BiPbSrCaCuO계 초전도체의 X선 회절패턴

Fig. 6. X-ray diffraction patterns of BiPbSrCa-CuO superconducting system of varing sintering times, spread volume ratio 1:0.6 (a) 24 h. (b) 120 h. (c) 210 h.

mixed phase peak almost disappeared around 760 ℃ (Fig. 7b), and the low phase peak (0010, 0012, 0016) appeared around 820 ℃ (Fig. 7c). After 50 hours, the low and some high Tc phase peaks appeared (Fig.7d). When the samples sintered for 210 hours, their low Tc phases almost disappeared. The high Tc phase was the major part. Long sintering (above 200 hours) was needed to develop the whole high superconducting phase in the inner particles.

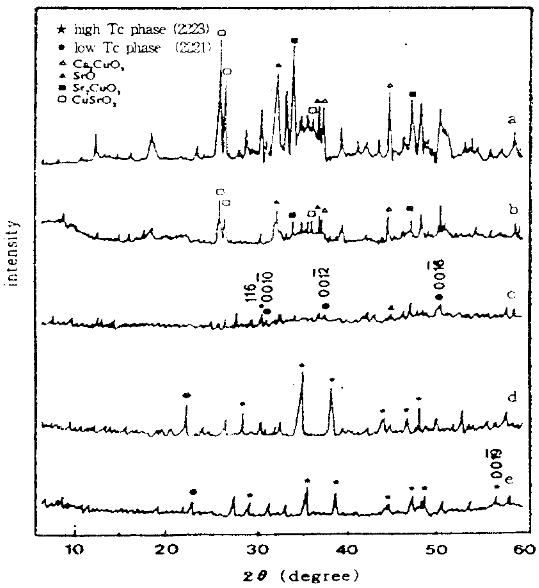


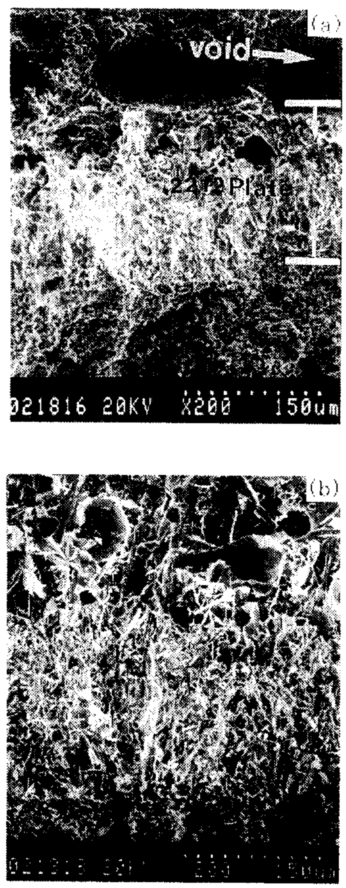
그림 7. BiPbSrCaCuO계 초전도체의 각 소결과정에 따른 X선 회절패턴 (도포비 1:0.6, 조성비 A: $Sr_2Ca_2Cu_2O_x$, B: $Bi_{1.9}Pb_{0.5}Cu_3O_y$)

Fig. 7. X ray diffraction patterns with each stage of sintering process at boundary surface of BiPbSrCaCuO superconducting system (spread volume ratio 1:0.6, composition A : $Sr_2Ca_2Cu_2O_x$, B : $Bi_{1.9}Pb_{0.5}Cu_3O_y$) (a) before sintering (b) 760 ℃ (c) 820 ℃ (d) 50 h. (820 ℃) (e) 210 h. (820 ℃)

3-3. SEM observations

The effects of spread volume ratio, sintering temperature and sintering time on phase formation were observed throughout the SEM. Fig. 8 shows the fracture section(It was cut in perpendicular direction of the sample) depending on spread volume of B sample ($Bi_2Pb_{0.3}Cu_2O_y$). A little amount of plate-like grains was observed in a little spread volume (Fig. 8a). Grain size of plate-like structure became gradually large with increasing spread volume (Fig. 8b). Also, Fig. 8c having spread volume of 1 : 0.6 shows that the plate-like grains as characteristic of typical Bi superconducting system were grown through diffusion process and initial penetration of B samples by melting.

Fig. 9 shows the fracture section depending on sintering time with the spread volume 1 : 0.6 at 820 ℃. When the sample was sintered for 24 h. (Fig.9a), the reaction was low. With increase of sintering time (Fig. 9b), the grain became the plate like shape little by little. Fig. 9c having sintering time of 210 h. showed mostly the plate-like structure. We found that superconducting phase growth was dependent on sintering time. On the other hand, SEM



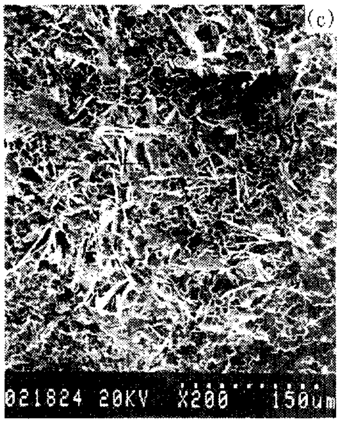
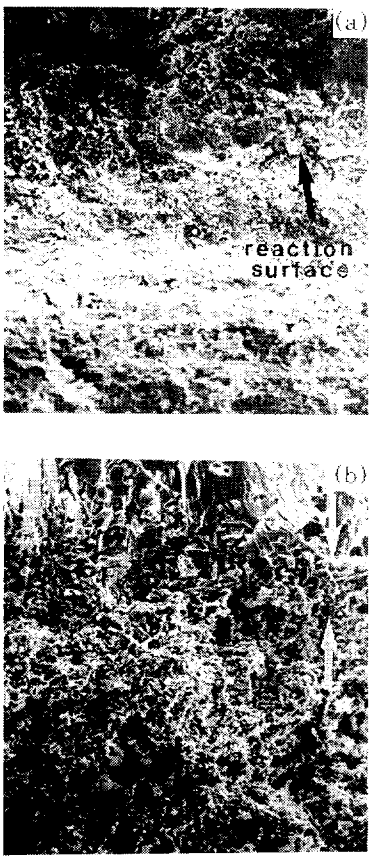


그림 8. 820℃에서 210시간 소결한 BiPbSrCaCuO계 초전도체의 도포비에 따른 SEM 사진

Fig. 8. SEM micrographs of BiPbSrCaCuO superconducting system of varing spread volume ratios sintered at 820 ℃ for 210 h. (a) 1 : 0.2 (b) 1 : 0.4 (c) 1 : 0.6

그림 9. 도포비 1 : 0.6, 소결온도 820℃에서 소결시간에 따른 BiPbSrCaCuO계 초전도체의 SEM사진

Fig. 9. SEM micrographs of BiPbSrCaCuO superconducting system of spread volume ratio 1:0.6, sintering temperature 820 ℃. for varing times. (a) 24 h. (b) 120 h. (c) 210 h.



observations of the specimen having sintering time over 210h. showed the same patterns as that of 210 h.

In the fixed conditions (sintering temp. 820 ℃, good condition [table 1]), the upper layer (Fig. 10) and fracture section (Fig. 11) of sintered samples of each step were observed by the SEM. The unsintered fine powder of the upper layer (Fig. 10a) was densely formed owing to compression of press machine Bi, Pb elements having a low melting temperature at 760 ℃ as shown in Fig. 10b formed a plate shape. The specimen (Fig. 10c) observed at 820 ℃ contained grain particles having bulk shape through interdiffusion, the liquid phase and particles were diffused with each other as well. Fig. 10d representing 1 hour after sintering process, showed that the grains grew up gradually and some grains penetrated into the inside. The samples had larger grain size and the voids owing to vacancies of element through interaction with increasing sintering process of 50 hours (Fig. 10e) We thought that the grain size somewhat decreased, because the element from the developed grain was separated and diffused with increasing sintering time (Fig. 10f).

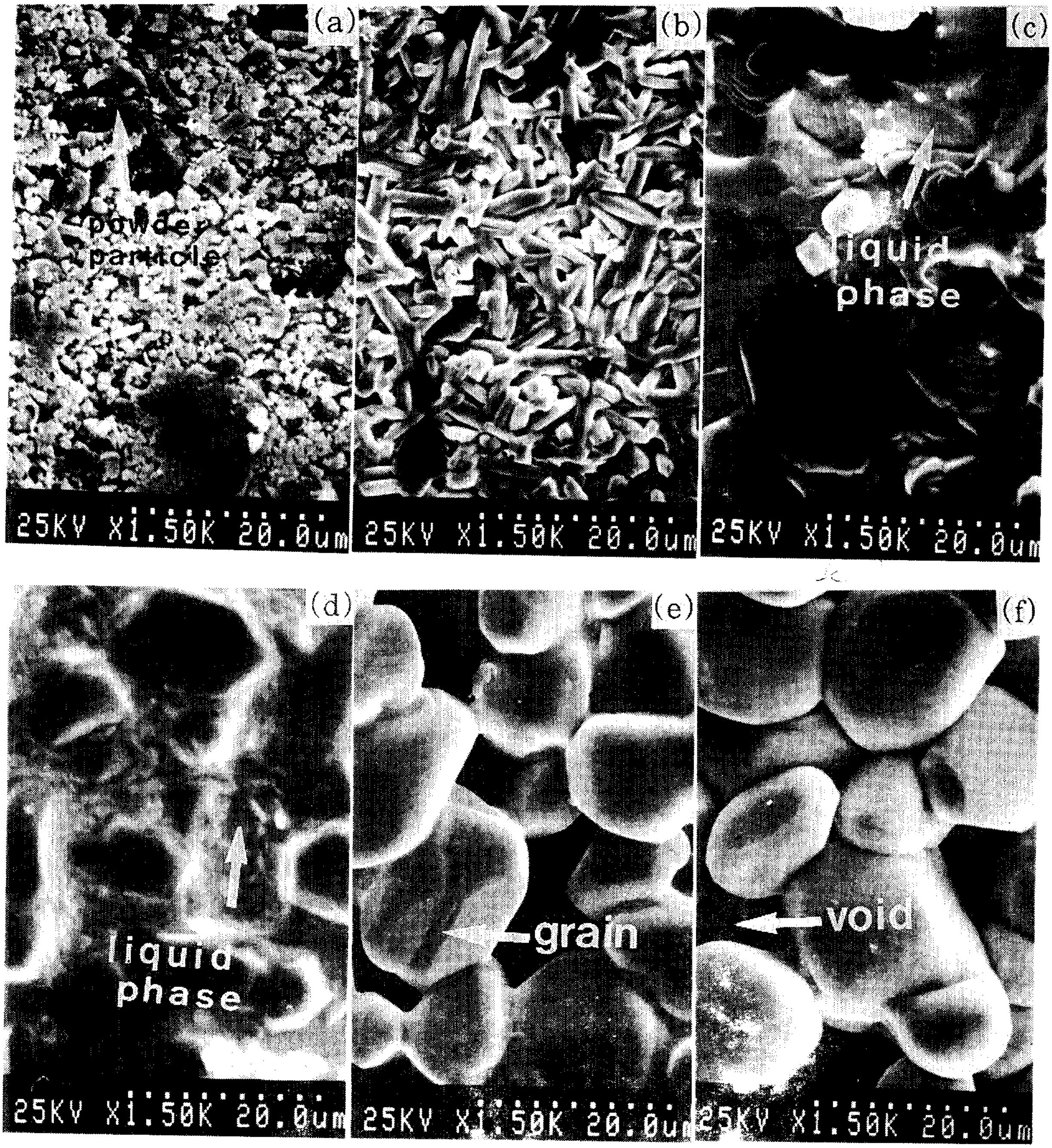


그림 10. BiPbSrCaCuO계 초전도체의 각 소결과정에 따른 표면의 SEM 사진 (소결시간 820℃, 도포비 1:0.6, 조성비 A : $Sr_2Ca_2Cu_2O_x$, B : $Bi_{1.9}Pb_{0.5}Cu_3O_y$)

Fig. 10. SEM images of upper surface with each stage of sintering process of BiPbSrCaCuO superconducting system (sintering temperature : 820 ℃, spread volume ratio 1:0.6, composition rate : A: $Sr_2Ca_2Cu_2O_x$, B: $Bi_{1.9}Pb_{0.5}Cu_3O_y$).

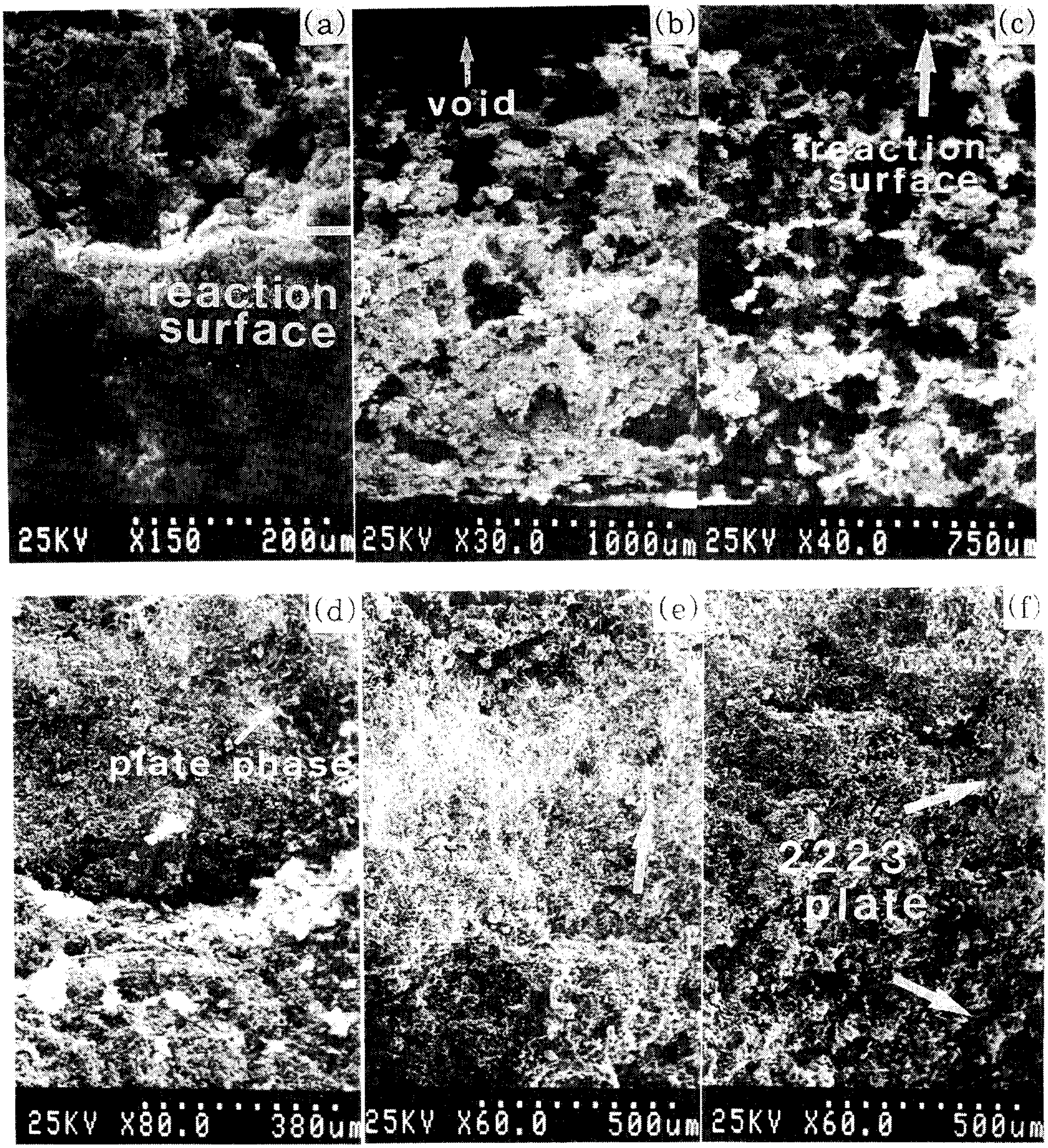


그림 11. BiPbSrCaCuO계 초전도체의 각 소결과정에 따른 시편 파단면의 SEM 사진
(소결시간 820℃, 도포비 1:0.6, 조성비 A : $Sr_2Ca_2Cu_2O_x$, B : $Bi_{1.9}Pb_{0.5}Cu_3O_y$)

Fig. 11. SEM images of fracture surface with each stage of sintering process of BiPbSrCaCuO superconducting system (sintering temperature : 820 ℃, spread volume ratio 1:0.6, composition rate : A: $Sr_2Ca_2Cu_2O_x$, B: $Bi_{1.9}Pb_{0.5}Cu_3O_y$).
(a) before sintering (b) 760 ℃ (c) 820 ℃ (d) 1 h. (e) 50 h. (f) 210 h.

Fig 11 showed that the liquid phase diffused to the upper layer before sintering (Fig. 11a), and the voids generated in the upper layer at 760 - 820 ℃ (Fig. 11b,c). While the second phase diffused in the upper layer and the element of low layer reacted, a large voids (Fig. 11b) was generated owing to gas reaction in the rising sintering process. It disappeared in the ensuing sintering process. The number of voids increased but the size of voids decreased when the sintering time increased 1 hour in the upper layer of the fracture section. The plate phase was observed showing a small amount in the reacted boundary layer (Fig. 11d). When the sintering time increased to 50 hours (Fig. 11e), the high Tc phase was increased, and the plate-like phase was observed in fracture section except for the upper layer and a part of lower layer, also unreacted elements were partially observed in process of the diffusion (Fig. 11e). We found that the superconducting phases grew up all the inner section of the specimens throughout the long sintering time (210 hours, Fig. 11f).

4. Conclusions

In this paper, we have presented the new method by diffusion process of double-layer in which we fabricated high Tc superconductor, and we have examined the effects of the composition and sintering time using the diffusion of double layer samples. We obtained the following conclusions through the illustration of the stability of high temperature superconducting phase and the growth.

1. The good conditions of Bi(Pb)SrCaCuO superconducting system were spread volume ratio of 1 : 0.6, sintering time of 210 hours, composition rate of $Sr_2Ca_2Cu_2O_x$ (A sample), $Bi_{1.9}Pb_{0.5}Cu_3O_y$ (B sample) and critical temperature was 108 K in good conditions.

2. The second phase and low Tc phase (2212) were formed in the increasing temperature step with the composition A : $Sr_2Ca_2Cu_2O_x$, B : $Bi_{1.9}Pb_{0.5}Cu_3O_y$, sintering temperature : 820 ℃, but when the low Tc phase decreased, the volume % of the high Tc phase increased with the increasing sintering time.

3. The superconducting phase formed a liquid phase in the beginning of sintering process. Through the ensuing sintering process the plate-like superconducting phase was formed by interdiffusion of under layer particles.

4. The superconducting phase was generated by interaction of the low Tc phase and the second phase, and these generation reactions were active in the beginning. The samples were stable owing to plate-like superconducting structure. It needs approximately 200 hours for improvement of the critical temperature.

5. The liquid phase promoting generation and growth of the high Tc phase arose by partial melting in the rising temperature. The SrCaCuO layer of the samples has many voids due to the diffusion of the liquid phase from the BiPbCuO layer even though some have a relatively fine structure.

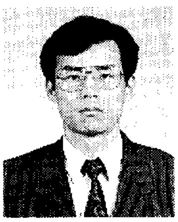
※ This work was supported by KOREA SANHAK foundation in 1995.

References

1. J.G. Bednorz and K.A. Muller, Z. Phys. B, vol. 3, pp. 379 (1987).
2. J.F. Schoolety, W. Holser and M. L. Choen, Phy. Rev. Lett., vol. 12, pp. 474 (1964).
3. J.W. Sleight, J.L. Gillson and F.E. Bierstedt, Solid state Commun., vol.17, pp. 27 (1975).
4. P. Chaudhari, R.H. Koh, R.B. Laibowitz, T.R. Meguire and R.J. Gambino, Phys, Rev. Lett., vol. 58, pp. 2687 (1987)
5. H. Maeda, Y. Tabajam, M. Fukutomi and T. Asno, Jpn. J. Appl. Phys., vol. 27, pp. L209 (1988).

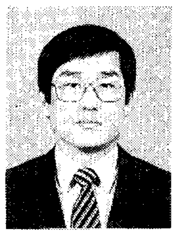
6. S.M. Green, C. Jiang, Yu. Mei and C. Politis, Phys. Rev., vol. B38, pp. 5016 (1988).
7. M. Takano, J. Takada, K. Oda and H. Mazaki, Jpn. J. Appl. Phys., vol. 27, pp. L1041 (1988).
8. L. Hongbao, L. Liezhao, Z. Ling and Z. Yuheng, Solid State Commun., vol. 69, pp. 867 (1989).
9. M.R. Chndrahood, I.S. Mulla and A.P.B. Sinha, Appl. Phys. Lett., vol. 55, pp. 1472 (1989).
10. H. Hoshizaki, S. Kawabata, N. Kawahara, Jpn. J. Phys., vol. 29, pp. 1444 (1990).
11. S. H. Choi, S.J. Park, H.S. Yu, H.G. Gang and B.S. Han, KIEE, vol. 43, pp. 795 (1993).
12. I. Mstsdubsra, H. Tanigawa, T. Ogura, H. Yamashita, M. Kinoshita, and T. Kawai, Jpn. J. Appl. Phys., vol. 28 pp. L1358 (1989).
13. T.H. Han, M.K. Kim, S.H. Choi, H.S. Choi and B.S. Han, KIEE, vol. 7, pp. 766 (1992).

저자소개



최효상

1967년 2월 21일생. 1989년 전북대학교 전기공학과 졸업. 1994년 전북대학교 전기공학과 졸업(석사). 현재 한전 전력연구원 에너지·환경고등연구소 초전도 분야 일반연구원. 주관심분야 : 초전도 재료 및 응용분야.



이중근

1954년 5월 16일생. 1989년 부산공업대 전기과 졸업. 1992년 경성대 산업공학과 졸업(석사). 1996년 현재 전북대학교 박사과정. 현재 한전 전력연구원 책임연구원. 주관심 분야 : 초전도 재료 물성 및 응용분야

정동철

1967년 8월 24일생. 1994년 전북대학교 전기공학과 졸업. 1995년 전북대 전기공학과 졸업(석사). 1996년 현재 전북대학교 박사과정. 주관심분야: 초전도 전자장 수치해석 및 응용.

한병성

1951년 12월 22일생. 1975년 전북대 공대 전기공학과 졸업. 1981년 동 대학 대학원 졸업(석사). 1988년 불란서 Louis Pasteur 대학 졸업(공박). 1982년-현재 전북대 전기공학과 교수. 불란서 CNRS 회원 및 방문교수. 1989년 UNESCO material center member. 1991년 IBM T.J. Watson center member. 현재 전북대학교 전기공학과 교수.