

## CHARACTERISTICS OF $Y_1Ba_2Cu_3O_{7-x}$ HIGH- $T_c$ SUPERCONDUCTOR PREPARED BY PARTIAL MELTING PROCESS

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**Abstract** — The superconducting  $Y_1Ba_2Cu_3O_{7-x}$  (123) and the  $Y_2Ba_4Cu_3O_8$  (211) powders in this study were prepared by pyrophoric synthesis method with  $Y_2O_3$  (99.9%),  $BaCO_3$  (99.9%), and  $CuO$  (99.9%) powders. Samples of 123 and 211 pellets were first prepared and then piled to have a 123/211/123 arrangement before a partial melting process was applied for phase change of the center piece (211) to 123 phase through a peritectic reaction. The process parameters were a melting temperature of 1,040-1,070°C and the mass of the 123 piece ranging from 0.4 to 1.2 g. The superconductivity, such as critical temperature ( $T_c$ ), and mass susceptibility ( $\chi$ ) of bulk 123 and 211 samples were measured by AC four point probe method and AC susceptometer, respectively. The experimental results can be summarized as follows: the best preparation condition in the range examined was a melting temperature of 1,060°C and mass ratio [123(A)/211(B)] of 2:1 with melting time of 30 minutes to yield the  $T_c$  of 88.5 K.

Key words :  $Y_1Ba_2Cu_3O_{7-x}$ ,  $Y_2Ba_4Cu_3O_8$ , Partial Melting Process, Piled Structure

### INTRODUCTION

The discovery by Bednorz and Muller [1986] of a La-Ba-Cu-O type superconducting oxide with a critical temperature ( $T_c$ ) above 35 K created a great sensation all over the world. Furthermore, the discovery of oxide superconductors such as the Y-Ba-Cu-O system by Chu et al. [1987] and Hor et al. [1987], the Bi-Sr-Ca-Cu-O system by Maeta et al. [1988], the Tl-Ba-Ca-Cu-O system by Sheng et al. [1988], and the Hg-Ba-Ca-Cu-O system by Putilin [1993] with  $T_c$  over 90 K, accelerated the impetus among scientists and engineers for an improved understanding of the superconducting mechanism and for practical applications. Recently, research efforts have been focused on the improvement of the critical current density ( $J_c$ ) and mechanical properties for purposes of application rather than on improvement of  $T_c$  or on the discovery of a new material. Although many other fabrication methods have been developed for high-temperature superconducting oxides, the solid state reaction method [Tachikawa et al., 1987; Obara et al., 1988] is the most widely used at present. However, since this method requires a series of processes of mixing, calcining and sintering, the reproducibility is not very good due to the complexity of the process parameters. Moreover, when some elements such as Ag, Al and Fe, etc. are substituted or added to improve their physical/chemical properties, it is difficult to obtain a homogeneous and fine powder due to the mechanical milling process. Thus, in this study, powders were prepared by a pyrophoric synthesis method, in which

liquid phase mixing and a pyrophoric reaction during the process allow homogeneous, uniform, and fine powders below 1  $\mu\text{m}$  average particle size [Kim et al., 1995, 1996; Park et al., 1998]. A more detailed description of this method can be found elsewhere [Kosuge et al., 1988; Bhattacharya et al., 1990].

For the application of bulk oxide superconductors, a substantial improvement in the  $J_c$  values is required. To achieve this goal various preparation techniques such as MTG (melt texture growth) [Jin et al., 1988], MPMG (melt powder melt growth) [Fujimoto et al., 1992], ZM (zone melting) [Yao et al., 1995], and PMP (partial melt process) [Miletich et al., 1993; Kim et al., 1993] etc. have been attempted with partial success.

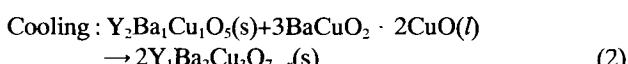
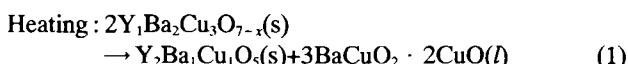
Among them, the PMP method reportedly yields large superconducting ( $Y_1Ba_2Cu_3O_{7-x}$ , 123) grains, good contacts of grain boundaries, and a superior susceptibility ( $\chi$ ) due to the fine dispersion of non-superconducting particles of submicron size in a superconducting phase [Lee et al., 1990]. The melt-texturing process is a technique making use of a peritectic reaction. The 123 specimen is first heated to decompose to 211 ( $Y_2BaCuO_8$ ) and a liquid phase and followed by cooling to react 211 and the liquid phase to make the 123 phase through the peritectic reaction, as can be seen in Fig. 1. The peritectic temperature is 1,040°C. In this process, however, since the 123 phase grows in the interface between 211 and the liquid phase and inevitably traps 211, this trapping 123 shields 211 from the liquid phase and the remaining liquid stays in the grain boundaries without playing a role as flux pinning centers [Sengupta et al., 1992]. That is known to be a major obstacle for a big increase in  $J_c$ . To circumvent this problem, the addition of 10-20 mol% of the 211 phase in 123 was tried out in vain due to a large shrinkage of specimen when fab-

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riated by use of the conventional partial melting process.

In this work, therefore, the samples of the 123 and 211 phase were first fabricated, then piled to have 123/211/123 arrangement, and finally a partial melting process was applied for a phase change of the center piece (211) to the 123 phase. The sandwich arrangement is to accommodate a large contact area and a symmetric phase formation due to mass transfers along with the interface regions. Also, to minimize the amount of remaining liquid phase, the weight of the 123 pellets of the specimen was varied from a much smaller amount to the stoichiometrically theoretical value on purpose.

The peritectic reaction mentioned above in a pseudo-binary phase diagram of  $\text{Y}-\text{Ba}-\text{Cu}-\text{O}$  system comes out as follows :



Through the heating reaction (1) in the temperature range of 1,050-1,100°C, the 123 disks partially melt and decompose into 211 and liquid phase. Since the formation and grain growth rate of the 123 phase is affected by a cooling rate in the reaction (2), the pellet must be cooled as slowly as possible to the temperature range of 950-1,010°C where the 123 grows.

The aim of this work is to investigate the mass transfer characteristics associated with the shift of the liquid phase between 123 and 211 phase in the partial melting process. The process parameters were the mass ratio between 123/211/123 pellets and the melting temperature.

## EXPERIMENTAL

In this work, the 123 and 211 powders were prepared by the pyrophoric synthesis method, using  $\text{Y}_2\text{O}_3$  (99.9%),  $\text{CuO}$  (99.9%) from Aldrich Chem. Co., and  $\text{BaCO}_3$  (99.9%) from Showa Co. These raw materials were mixed by the molar ratio of  $\text{Y} : \text{Ba} : \text{Cu} = 1 : 2 : 3$  for 123 and  $2 : 1 : 1$  for 211, respectively.

The 123 powder was pressed at  $200 \text{ kg/cm}^2$  into disks with a diameter of 15.35 mm and of various weights of 0.4, 0.6, 0.8, 1.0 and 1.2 g, respectively. The 211 disk with the same diameter and the fixed weight of 1.0 g was fabricated from 211 powder at  $300 \text{ kg/cm}^2$ . The disks of 123 and 211 phase were piled to have a 123/211/123 arrangement as shown in Fig. 1, and then heat-treated by a partial melting process.

Following the heat treatment schedule as illustrated in Fig. 2, the piled specimen was heated to 950°C at a heating rate of  $50^\circ\text{C}/\text{min}$ ; it stayed there for 12 hrs and then was heated again to the melting zone temperature (1,040, 1,050, 1,060, and 1,070°C, respectively) at a heating rate of  $100^\circ\text{C}/\text{min}$  and held for 30 min. The peritectic reaction [Eq. (1)] occurs here forming 211 plus liquid phase. The specimen was cooled to 1,000°C at a cooling rate of  $0.8^\circ\text{C}/\text{min}$  and cooled further to 980°C at the rate of  $0.1^\circ\text{C}/\text{min}$  to promote the formation of 123 phase following the reaction [Eq. (2)]. Annealing for the phase transition from tetragonal to orthorhombic was carried

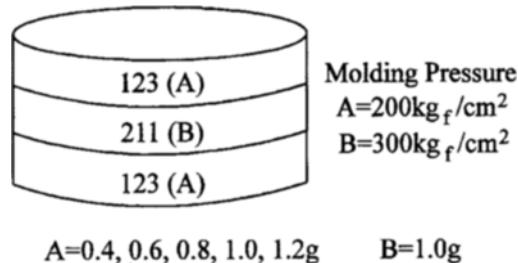


Fig. 1. Composition and preparation of 123(A)/211(B)/123(A) system specimen by partial melting process.

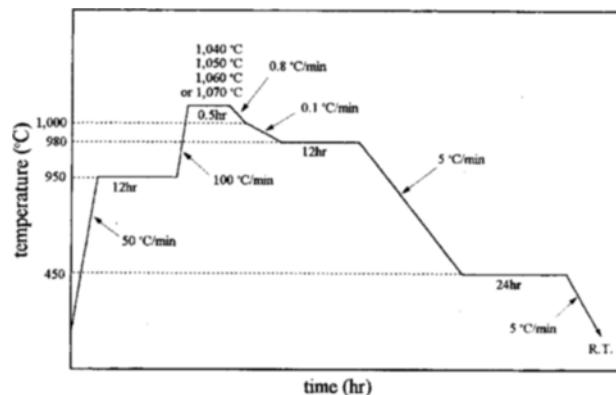


Fig. 2. Temperature programmed heat treatment schedule of 123(A)/211(B)/123(A) specimen by partial melting process.

out at 450°C for 24 hours under oxygen atmosphere at a flow rate of 150 ml/min and then cooled to room temperature.

The electric resistance was measured by the AC four-probe method using Ag-paste of a high conductivity. DC current of 1 mA was used for the measurement of resistance in the temperature range of 79 to 120 K. Temperature dependence of magnetic susceptibility of the specimens was surveyed at 0.1 Oe in the temperature range of 50 to 100 K with AC susceptometer (Lake shore 7000 series).

To investigate the crystal structure of the specimens, X-ray diffraction (Rigaku III/A type) was performed under the condition of 30 kV, 20 mA, scan speed:  $5^\circ/\text{min}$ , and  $2\theta=10-60^\circ$  with a  $\text{Cu}-\text{K}\alpha$  ( $\lambda=1.5418 \text{ \AA}$ ). The surface morphology and the particle size of the specimens were observed by SEM (scanning electron microscopy : Hitachi-650). The compositions of the samples were determined by EPMA (electron probe micro-analyzer : JEOL, JXA-8600).

## RESULTS AND DISCUSSION

### 1. Effect of 123(A) Weight Change

Table 1 lists the mass and molar ratios between 123 and 211 in the specimens before the partial melting process is applied.

Fig. 3 is the electrical resistivity vs. temperature curve for specimens with various 123(A) weights. With an increase in weight from 0.4 to 1.2 g, the  $T_{\text{co}}$  of 211(B) improved considerably. This result is obviously because of the increased amount of liquid phase  $3\text{BaCuO}_2 \cdot 2\text{CuO}$  formed through the decomposition of 123(A) on heating for increasing amount of 123(A) pel-

**Table 1. Mass and molar ratios between 123 and 211 pellets in the specimens**

Mass of 123(A)[g]	Mass ratio* (123:211)	Molar ratio (123:211)	mol% deficiency†
0.4	0.8:1	0.54:1	73.1
0.6	1.2:1	0.81:1	59.6
0.8	1.6:1	1.08:1	46.0
1.0	2.0:1	1.35:1	32.6
1.0	2.4:1	1.62:1	19.0
1.5	3.0:1	2.00:1	0

\*mass of 211(B) pellet is fixed at 1.0 g

†deficiency based on the theoretical 2:1 molar ratio between 123:211

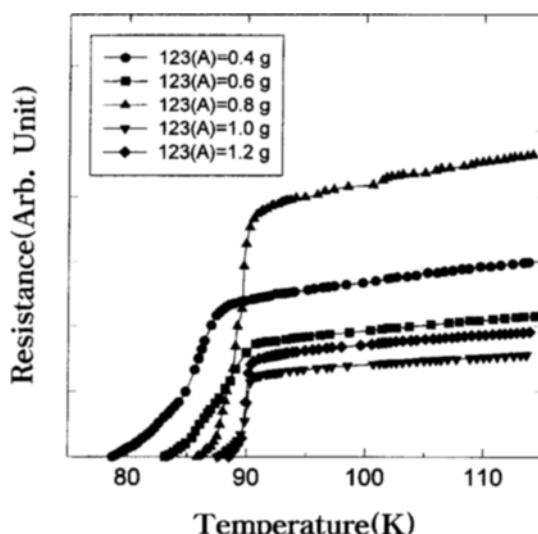


Fig. 3. Electrical resistance vs. temperature for the specimen 211(B) after heating at 1,060 °C for 30 min (211(B)=1.0 g).

lets, which acts as a reactant for the reaction [Eq. (2)] above in cooling. This increase, however, appears saturated over 0.8 g.

Figs. 4 and 5 are the X-ray diffraction patterns of the outer pieces (123) and those of the center piece (211), respectively. They were detached from the specimen after the partial melting process at 1,060 °C. The filled circles in Figs. 4 and 5 denote 123 phase and the open squares 211 phase. In both Figs. 4 and 5, the diffraction intensity of the 123 phase tends to gradually increase in accordance with the amount of 123(A) while the 211 phase decreases. In the case of outer pieces, it seems that when the amount of 123(A) in the piled pellet is small, much of the 123 transforms to 211 and liquid phase and all the liquid phase formed would transfer to the center piece 211(B), resulting in 211 as a dominant phase. However, when the 123 is abundant, only a portion of the liquid phase transfers to 211(B) and the 123 still remains as a majority phase. In the case of the center piece, however, since the 123 is forming in the interface between 211 and liquid, the 123 phase continuously increases as with the amount of liquid phase before saturated. The diffusion rate of the liquid phase through the 123 phase already formed to the 211 should

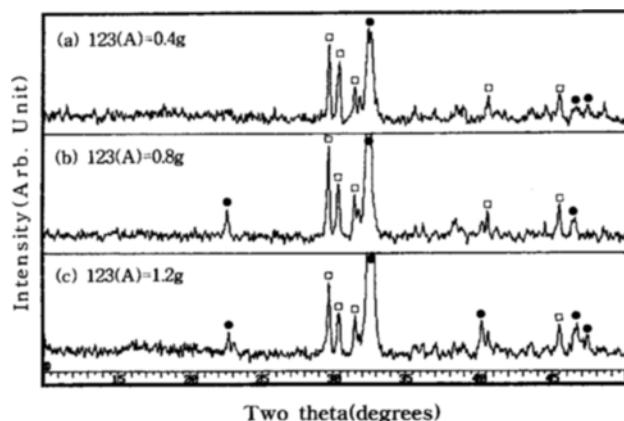


Fig. 4. X-ray diffraction patterns of specimen 123(A) after heating at 1,060 °C for 30 min.

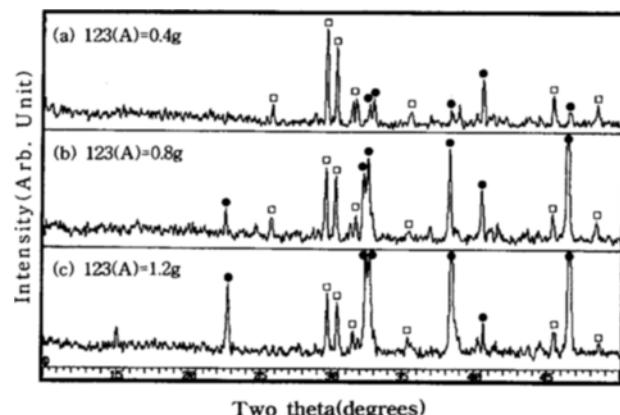


Fig. 5. X-ray diffraction patterns of specimen 211(B) after heating at 1,060 °C for 30 min.

be very slow, which is characteristic of a peritectic reaction.

These results indicate that a transport of liquid phase from the outer pieces to the center piece as well as from the interface to the 211 is the rate controlling step in this partial melting process. Viewed from the peritectic reactions of [Eq. (1)] and [Eq. (2)], the molar ratio of 2:1 between 123 and 211 pellets would be theoretically optimum. However, due to the restriction of slow diffusion, the specimen with mass ratio of 2:1 for 123/211 yielded a best result in the range examined.

Figs. 6 and 7 show temperature dependences of real (X') and imaginary (X'') components, respectively, of susceptibility for 211(B) pellets fabricated by partial-melting method at 1,060 °C with various weights of 123(A). As can be seen from Fig. 6, susceptibility characteristics tend to increase with the increase of 123(A) weight and are considerably enhanced at weight over 1.0 g. The T<sub>c, onset</sub> of all the specimens were similar with about 90.5 K.

Fig. 8(a) is cross-sectional SEM micrograph of 123(A)/211(B)/123(A) samples fabricated by partial melting process at 1,070 °C. After sintering, cavities were greatly increased in the region of 123(A), while a denser structure was obtained in the 211(B) region. Fig. 8(b) shows the magnified SEM photograph of the 211(B) region in Fig. 8(a). The weights of 123(A) and 211(B) pellets were all 1 g. It can be said that

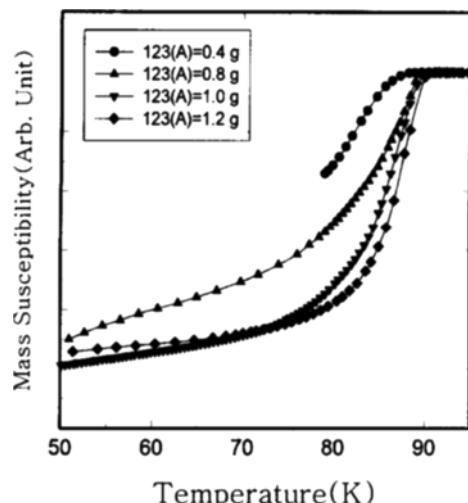


Fig. 6. Temperature dependence of real ( $X'$ ) component of susceptibility for 211(B) pellet after partial melting process is applied at  $1,060\text{ }^\circ\text{C}$  for 30 min.

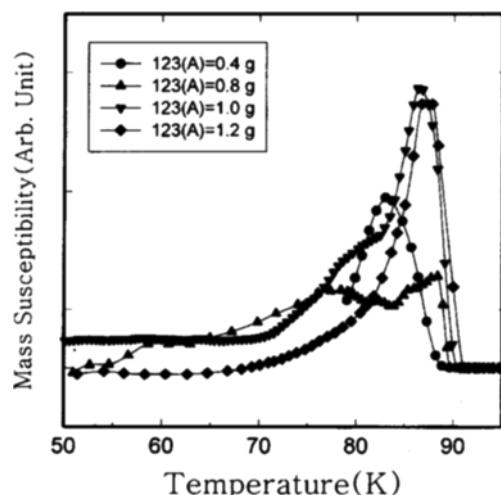


Fig. 7. Temperature dependence of imaginary ( $X''$ ) component of susceptibility for 211(B) pellet after partial melting process is applied at  $1,060\text{ }^\circ\text{C}$  for 30 min.

the coupled pellet of 123(A)/211(B)/123(A) has a larger grain growth and a very dense structure compared to those of a single pellet fabricated by the conventional solid-state reaction method. We believe that a larger grain growth and denser structure are mainly attributed to the liquid-solid reaction involved in this method instead of the solid-solid reaction in the conventional solid-state reaction method. We also expect that the larger grain size with a higher density would improve the other superconducting characteristics such as  $J_c$  value and mechanical flexibilities etc., which are yet to be done.

Fig. 8(b) and 9(a) are typical cross-sectional SEM micrographs of 123(B) and 211(A) pellets, respectively, after the partial melting process at  $1,070\text{ }^\circ\text{C}$  for 30 min. The EPMA spectra of grain [A] in Fig. 9(a) are shown in Fig. 9(b). The result of EPMA shows that Y-Ba-Cu composition is changed from the existing mole ratio of 1:2:3 to 1.8:1.2:1.2, which is caused by mass transfer of  $\text{BaCuO}_2 \cdot 2\text{CuO}$ . The

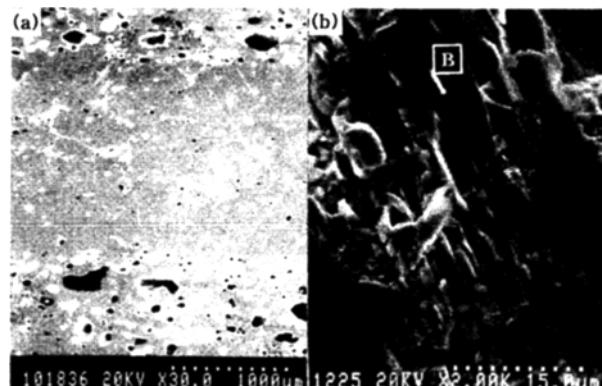


Fig. 8. Cross-sectional SEM micrographs of 211(B) specimen after partial melting process is applied at  $1,070\text{ }^\circ\text{C}$  for 30 min : (a)  $\times 30$ , (b)  $\times 3,000$ , and (c) EPMA spectra of grain [B].

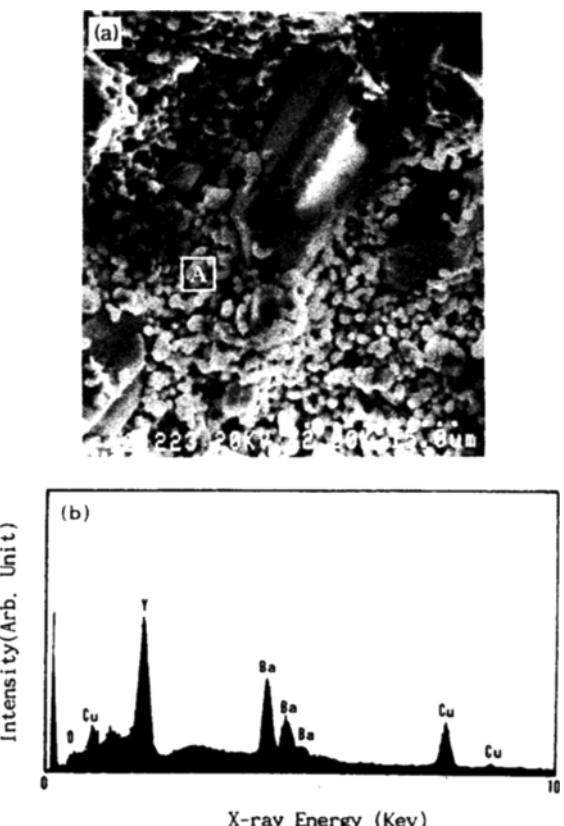


Fig. 9. (a) Cross-sectional SEM micrograph of 123(A) specimen after partial melting process is applied at  $1,070\text{ }^\circ\text{C}$  for 30 min, and (b) EPMA spectra of grain [A].

EPMA analysis of Fig. 8(c) for the [B] grain of Fig. 8(b) indicates the Y-Ba-Cu composition of 1:1.6:2.3, which reveals by simple algebra that about 80 % phase transition has occurred from the 211 to the 123 phase.

## 2. Effects of Melting Temperature

In this study we investigated the effects of melting temperature on superconducting characteristics in terms of mass transfer rate of liquid phase formed during the partial melting process from the outer to the center piece. The specimens were prepared as follows: 1.0 g of fixed weight of 123(A) and 211(B); 30 minutes of holding time of the second stage in heat treatment schedule of Fig. 2. The melting temperature was varied as a process parameter to 1,040, 1,050, 1,060, and 1,070 °C, respectively.

Fig. 10 shows X-ray diffraction patterns of specimen 123(A) fabricated at various melting temperatures. Except for sample (a) fabricated at 1,040 °C, both 123 and 211 phases appear and 211 intensity gradually increases as the melting temperature increases from 1,050 °C. This means that the phase transition from the 123 to the 211 phase due to mass transfer increases with an increase of melting temperature over 1,050 °C.

Fig. 11 shows X-ray diffraction patterns of specimen 211(B) under the same experimental condition with Fig. 10. The peaks of sample (a) fabricated at 1,040 °C show that 211 phase is dominant, which can be explained by a small amount

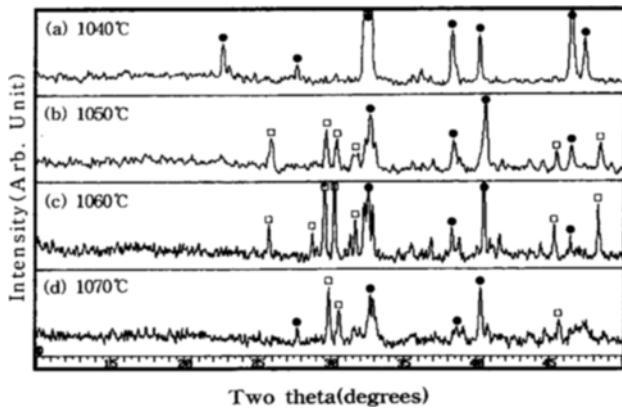


Fig. 10. X-ray diffraction patterns of 123(A) specimen after heating at various temperatures for 30 min.

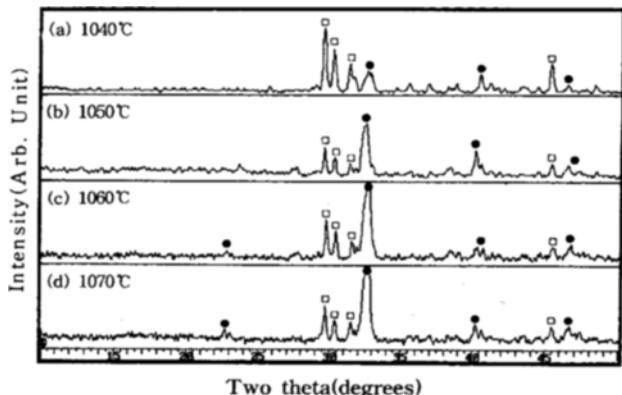


Fig. 11. X-ray diffraction patterns of 211(B) specimen after heating at various temperatures for 30 min.

of mass transfer at this temperature, while the peaks of samples fabricated over 1,050 °C show that 123 phase is a majority phase other than 211 phase.

Fig. 12 displays an electrical resistance vs. temperature curve for the center piece of 211(B) after being treated at various melting temperatures of 1,050, 1,060, and 1,070 °C, respectively. The specimen prepared at 1,040 °C does not show superconductivity at the boiling temperature of liquid nitrogen (77 K), mostly due to too small an amount of 123 phase formed, while the other specimens show similar  $T_{c, onset}$  values of 90-91 K. The  $T_{c, o}$  values of the specimens fabricated at 1,060 and 1,070 °C were 88.5 and 88 K, respectively, but the one at 1,050 °C had a slightly lower value of  $T_{c, o}$ .

Thus, the most proper melting temperature for the formation of 123 superconducting oxide turned out to be 1,060-1,070 °C.

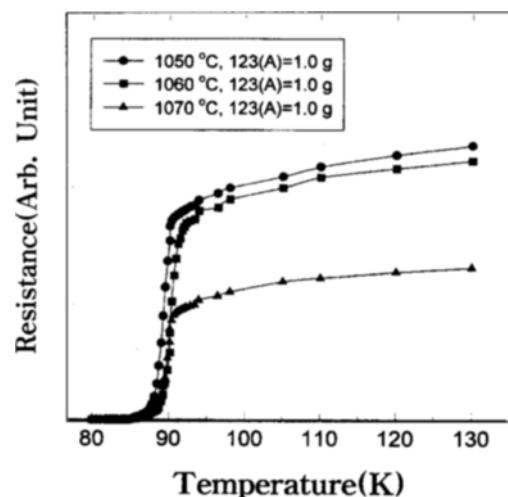


Fig. 12. Electrical resistance vs. temperature for 211(B) specimen after heating at various temperatures for 30 min.

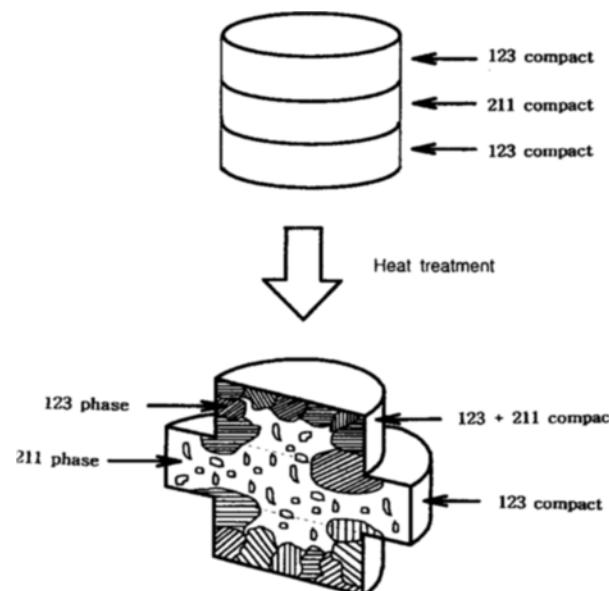


Fig. 13. Schematic drawing of the transition process from 211 to 123 phase in the center specimen.

Fig. 13 depicts the transition of the 211 center piece to 123 phase by the partial melting process. The merits of this piled structure of 123/211/123 over the 211/123 system are as follows: reaction interface can be doubled to promote homogeneous mass transfer of liquid phase through the peritectic reaction from the outer pieces to the center without rotation of the specimens during the process of sintering and annealing, and also the formation of 123 superconducting phase in addition to homogeneous distribution of 211 particles will be more elevated.

## CONCLUSIONS

A Y-Ba-Cu-O system high temperature superconductor with a coupled pellet of 123/211/123 arrangement was fabricated by partial melting process, and effects of 123(A) weight and melting temperature were investigated.

The experimental results can be summarized as follows:

1. The mass transfer of liquid phase was best carried out at a melting temperature of 1,060 °C for the specimen with a mass ratio of 2:1 for 123/211. A  $T_{c, onset}$  value of 90-91 K and a  $T_{c, o}$  value of 88-88.5 K were obtained.
2. It can be seen that the liquid phase of  $3BaCuO_2 \cdot 2CuO$  transfers toward the center region of 211(B) from 123(A) over 1,050 °C and that this transport of liquid phase is the rate-controlling step in the partial melting process.
3. In the resulting center piece, about 80 % phase transition has occurred from 211 to 123 phase and the 211 phase exists as a second phase.

## ACKNOWLEDGMENT

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## REFERENCES

Bednorz, J. G. and Muller, K. A., "Possible High  $T_c$  Superconductivity in the Ba-La-Cu-O System", *Z. Phys.*, **B64**, 189 (1986).

Bhattacharya, D., Pathak, L. C., Mishra, S. K., Sen, D. and Chopra, K. L., "Pyrophoric Synthesis Technique for Multicomponent High-Temperature Superconductors", *Appl. Phys. Lett.*, **57**(20), 2145 (1990).

Chu, C. W., Hor, P. H., Meng, R. L., Gao, L., Huang, Z. J. and Wang, Y. Q., "Evidence for Superconductivity above 40 K in the La-Ba-Cu-O Compound System", *Phys. Rev. Lett.*, **58**(4), 405 (1987).

Fujimoto, H., Murakami, M. and Koshizuka, N., "Effect of  $Y_2BaCuO_5$  on Fracture Toughness of YBCO Prepared by a MPMG Process", *Physica C*, **203**, 103 (1992).

Hor, P. H., Gao, L., Meng, R. L., Huang, Z. J., Wang, Y. Q., Forster, K., Vassiliou, J., Chu, C. W., Wu, M. K., Ashburn, J. R. and Torga, C. J., "High-Pressure Study of the New Y-Ba-Cu-O Superconducting Compound System", *Phys. Rev. Lett.*, **58**(9), 911 (1987).

Jin, S., Tiefel, T. H., Sherwood, Davis, M. E., Van Dover, R. B., Kammlott, G. W., Fastnach, R. A. and Keith, H. D., "High Critical Currents in Y-Ba-Cu-O System", *Appl. Phys. Lett.*, **52**(13), 2174 (1988).

Kim, C. J., Kim, K. B., Chang, I. S. and Won, D. Y., "The Effect of  $Y_2Ba_1Cu_1O_5$  Addition on Microstructure and Formation of Microcracks in the Partially Melted Y-Ba-Cu-O Oxides", *J. Mater. Res.*, **8**(4), 699 (1993).

Kim, Y. S., Park, J. S., Chung, B. W. and Shin, H. S., "Corrosion Behavior of High-Temperature Superconductor  $YBa_2Cu_{3-y}Ag_yO_{7-x}$  in the Presence of Water", *Korean J. Chem. Eng.*, **12**(5), 563 (1995).

Kim, Y. S., Yang, S. W., Park, J. S. and Shin, H. S., "Superconductivity of  $YBa_2Cu_{3-y}Ag_yO_{7-x}$  Manufactured by Pyrophoric Synthetic Method", *J. of Korean Ind. & Eng. Chemistry*, **7**(4), 639 (1996).

Kosuge, M., Okai, B., Takahashi, K. and Ohta, M., "Preparation and Physical Properties of  $Y_{1-x}Ca_{1.1}Ba_{2-0.1x}Cu_3O_x$ ", *Jpn. J. Appl. Phys.*, **27**(6), L1022 (1988).

Lee, H. G., Kwon, S. C., Lee, H. J., Lee, J. C., Chan, I. S., Rim, C. S., Kim, C. J. and Won, D. Y., "Preparation of High Magnetization YBaCuO Bulk Superconductor by Quasi-melt Process", *Advance in Superconductivity III, Proceedings of the 3rd International Symposium on Superconductivity (ISS'90)*, 789 (1991).

Maeda, H., Tanaka, Y., Fukutomi, M. and Asano, T., "A New High- $T_c$  Oxide Superconductor without a Rare Earth Element", *Jpn. J. Appl. Phys.*, **27**(2), L209 (1988).

Miletich, R., Murakami, M., Preisinger, A. and Weber, H. W., "Microstructural Characteristics of Melt-powder-melt-grown  $YBa_2Cu_3O_{7-x}$  Crystals", *Physica C*, **209**, 415 (1993).

Obara, H., Oyanagi, H., Murata, K., Yamasaki, H., Ihara, H., Tokumoto, M., Nishihara, Y. and Kimura, Y., "Superconductivity, Structure and Oxygen Content of Fe-Doped  $Ba_2YCu_3O_y$ ", *Jpn. J. Appl. Phys.*, **27**(4), 603 (1988).

Park, J. S., Kim, Y. S., Yang, S. W., Kim, C. Y. and Shin, H. S., "Effect of pH Pyrophoric Synthetic Solution on the  $YBa_2Cu_3O_{7-x}$  Superconducting Phase Formation Kinetics", *J. of Korean Ind. & Eng. Chemistry*, **9**(2), 165 (1998).

Putilin, S. N., Antipov, E. V., Chmaissem, O. and Marezio, M., "Superconductivity at 94 K in  $HgBa_2CuO_{4+\delta}$ ", *Nature*, **362**, 226 (1993).

Sengupta, S., Shi, D. and Wang, Z., "Effect of  $Y_2BaCuO_x$  Precipitates on Flux Pinning in Melt-Processed  $Y_1Ba_2Cu_3O_x$ ", *Physica C*, **199**, 43 (1992).

Sheng, Z. Z. and Hermann, A. M., "Bulk Superconductivity at 120 K in the Tl-Ca-Ba-Cu-O System", *Nature*, **332**, 138 (1988).

Tachikawa, K., Sadakata, N., Sugimoto, M. and Kohno, O., "Fabrication of Superconducting Y-Ba-Cu-O Oxide Through an Improved Diffusion Process", *Jpn. J. Appl. Phys.*, **27**(8), L1501 (1987).

Yao, X., Sumida, M. and Shiohara, Y., "Influences of Oxygen Partial Pressure on YBCO Grain Growth by a Zone Melting Method", *J. Mater. Res.*, **11**(11), 2711 (1996).