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Development of Large Scale $YBa_2Cu_3O_{7-x}$ Superconductor with Plastic Forming

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1. Introduction

As superconducting oxides with a critical temperature above 77 K were discovered in 1986[1], subsequent developments and research into superconducting materials such as $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2CaCu_2O_x$ have been widely carried out. Depending on the application, superconducting materials have been prepared as pellets, wires, or films. In order to synthesize products, numerous approaches have been tried using a variety of synthesis technologies, such as melt-powder-melt growth (MPMG)[2], and quench and melt growth (QMG)[3]. In order to produce a large bulk sample with these methods, the equipment must be remodeled to fit the sample size. This limits the size of the samples that can be produced. For thin films, several methods have been used such as the sol–gel method[4], metalorganic chemical vapor deposition (MOCVD)[5], pulsed laser deposition[6]. However, it is difficult to produce thick and large samples with various three-dimensional structures by these methods. Large bulk superconducting materials for making magnetic shielding for use in magnetic resonance imaging (MRI) cannot be produced by the above techniques. Therefore, a technique for easily and inexpensively making a large bulk superconductor is highly desired.

Plastic forming is very simple method and has been widely used for producing ceramics. However, there have been few papers about the preparation of bulk superconductor with using plastic forming. In the plastic forming, the slurry is prepared with kneading the mixture of ceramic powder, binder, dispersant and solvent. Polyvinyl alcohol (PVA), poly ethylene glycol, clay, sodium silicate and alumina colloid are used as the organic or inorganic binder. The addition of several % these binders to the slurry improves the forming performance of the green body and the homogenization properties of the sintered sample. Surfactants or sodium diphosphate are used as organic or inorganic dispersant. After firing, the organic binder and dispersant above described may be left in the sample as some kind of impurity. It is also known that the residual carbon and other impurities exist along the grain boundary and influence the electrical and mechanical properties. It was reported that the residual carbon decreased the superconducting properties, especially the critical current density [7]. Therefore, the plastic forming has not been used to make the bulk superconductor sample, because the used slurry includes many impurities.

When the large bulk superconductor samples are made by the plastic forming, we think next matters are important.

1. Making the particle size of ceramic powders the same size.
2. Making the particle size of inorganic binder the same size.
3. Removing useless materials (act as impurities) from the slurry.

In this book, we introduce how to make the large scale $YBa_2Cu_3O_{7-x}$ superconductor with plastic forming.

2. Preparation and characterization

2.1 Preparation process for $YBa_2Cu_3O_{7-x}$ slurry and bulk $YBa_2Cu_3O_{7-x}$ sample and measurements.

Figure 1 shows the preparation procedure for the $YBa_2Cu_3O_{7-x}$ bulk sample. Calcined $YBa_2Cu_3O_{7-x}$ powder was prepared by firing a mixture of Y_2O_3 (purity 99.99%), $BaCO_3$ (purity 99.9%), and CuO (purity 99.99%) at 1223 K in air. The $YBa_2Cu_3(OH)_x$ precursor was synthesized by hydrolyzing an ethanol solution containing $Y(OC_3H_7)_3$ (purity 99.9%), $Ba(OC_3H_7)_2$ (purity 99.9%), and $Cu(CH_3COO)2$ (purity >95%) at a molar ratio of 1:2:3. The precursor was refined with absolute ethanol after precipitation and filtration. Sol solutions were prepared by suspending the refined precursor in the solution at various PVA concentrations using an ultrasonic cleaner. PVA with an average molecular weight of 22 000 (degree of polymerization5500) was dissolved in warm water (at 40 – 45°C) and the solution was equilibrated to room temperature[8].

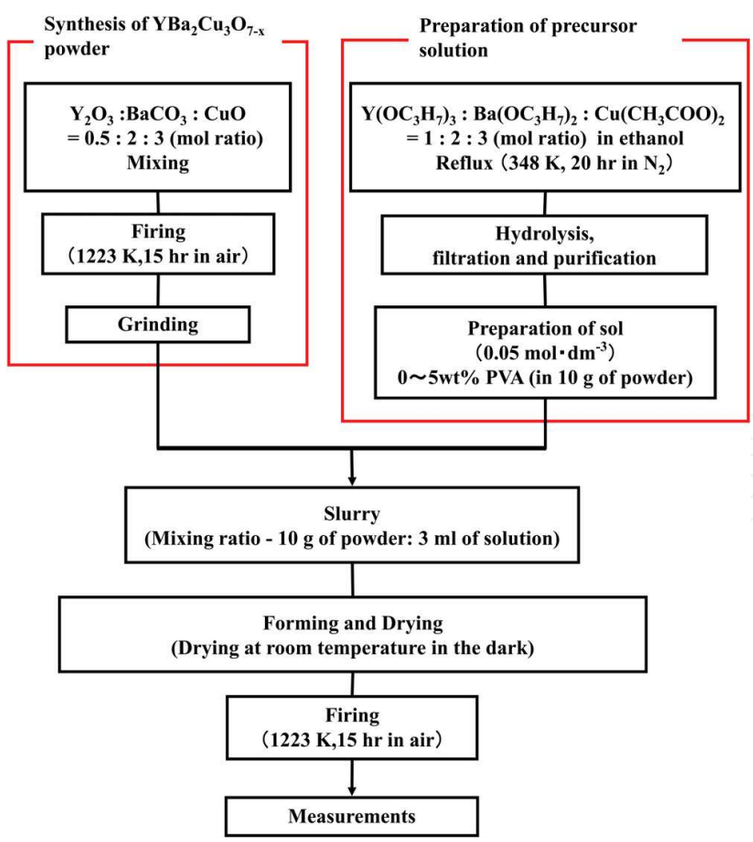

Fig. 1. Preparation procedure for YBa2Cu3O7-x slurry and bulk sample.

Green sheet samples (about 80 mm x 80 mm x 3 mm) were made using the slurry prepared by mixing 10 g of $YBa_2Cu_3O_{7-x}$ powder (average diameter 0.15 mm) and 3 ml of 0.05 mol/dm^3 precursor solution (average diameter of precursor particle: 380 nm) (kneading time: 50–60 min). After being dried in the shade at room temperature for 6 days, the sample was fired in an electric furnace at 1223 K for 15 h in air. The heating rate was set to about 50 K/h and the cooling rate to about 90 K/h up to about 440 K.

The crystal structures of the samples were measured by the X-ray diffraction (XRD) method (Rigaku Co., Ltd., Mini Flex, Tokyo, Japan) using CuKα1(0.154 nm) radiation. The surface morphology and composition of the samples were examined using a scanning electron microscope (SEM) (Hitachi High-Technologies Corporation, S-3500N, Tokyo, Japan) at an accelerating voltage of 15 kV. Standard four-probe DC electrical measurements using a 10 mA constant current were carried out in a flow cryostat operated over a temperature range of 50–300 K in a vacuum of 10^{-4} Torr. The degrees of dependence of the Jc on the magnetic field strength were evaluated using magnetization curves (M–H curves) and the Bean equation [Jc=30(⊿MH/d), in which ⊿MH is the width of M–H hysteresis and d is the sample thickness]. M–H curves were measured using a vibrating sample magnetometer (VSM) at 77 K[9]. The magnetic field was changed from -1.0 to +1.0 T. The values plotted in the figure are the average values for at least three and up to five samples that were grown under the same set of conditions.

2.2 The effect of PVA on the shaping of samples

Figure 2 shows photographs of green sheets and sintered samples prepared from the slurry with (1) 0 and (2) 1 wt% PVA.

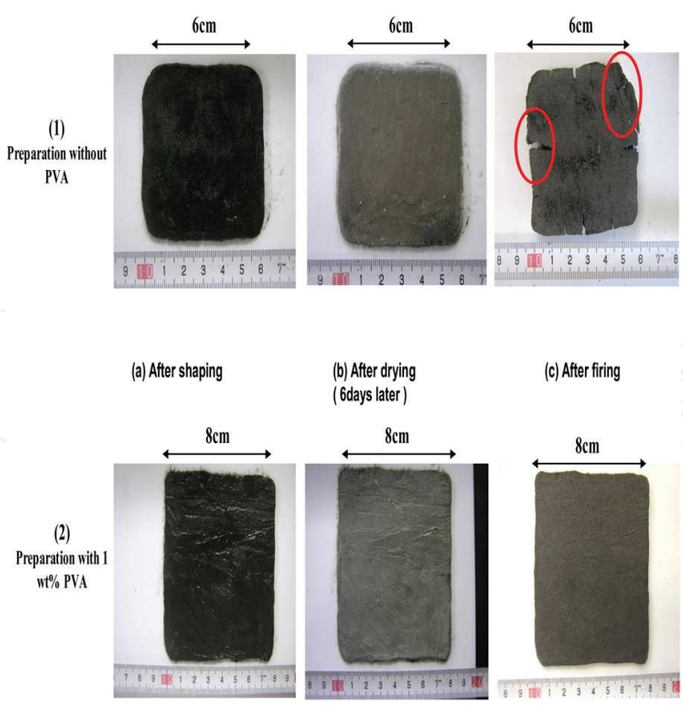

Fig. 2. The effect of PVA on the shaping of sample. Photographs of the samples prepared from the slurry containing (1) 0 and (2) 1 wt% PVA at (a) after shaping, (b) after drying (6 days later) and (c) after firing.

From photographs in Fig. 2(1), many crazes were observed on the surface of the dry green sheet (see in Fig. 2(1)(b)). After firing(see in Fig. 2(1)(c)), many large cracks were observed on the surface and near peripheral region.
On the other hand, in Fig. 2(2), no crazes and no cracks were seen with the naked eye for the dry green sheet(see in Fig. 2(2)(b)) and the sintered sample(see in Fig. 2(2)(c)).
These results indicate that crack generation can be considerably reduced by adding a small amount of PVA to the slurry.

2.3 The effect of PVA on the product

Figure 3 shows the X-ray diffraction patterns of samples prepared from the slurry with (a) 0 wt% and (b) 1 wt% PVA. In these X-ray diffraction patterns, 18 diffraction peaks are observed at 2θ= 22.81, 27.71, 27.91, 30.61, 32.51, 32.81, 38.51, 40.31, 46.51, 47.51, 51.41, 52.51, 54.91, 58.21, 58.71, 62.71, 68.11 and 68.71, corresponding to the (030), (120), (021), (040), (130), (031), (050), (131), (200), (002), (151), (160), (070), (161), (132), (241), (260), and (081) planes of orthorhombic $YBa_2Cu_3O_{7-x}$, respectively[10]. These results indicate that adding a small amount of PVA to the slurry has no marked influence on the final product in X-ray resolution.

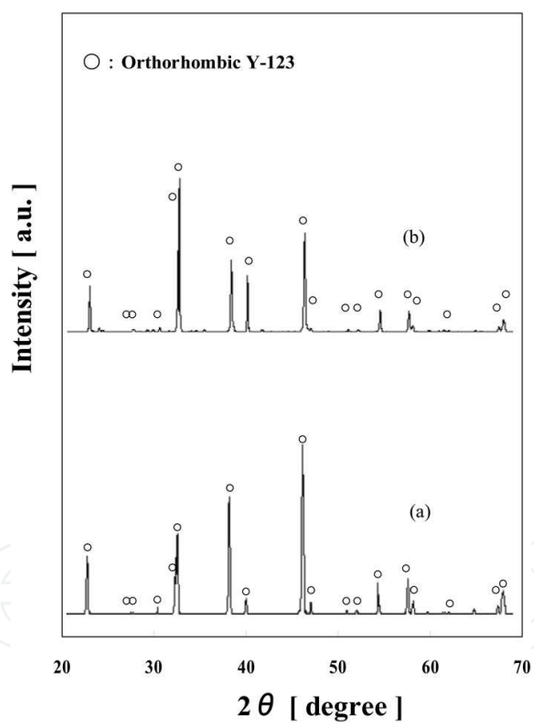

Fig. 3. X-ray diffraction patterns of the sheet samples prepared from the slurry with various PVA concentrations: (a) 0 and (b) 1 wt%.

2.4 Effect of adding PVA on the superconducting properties

Figure 4 shows the temperature dependence of electrical resistance for the samples prepared from the slurry with (a) 0 wt% and (b) 1 wt% PVA concentration. It can be seen that, for both samples, the electrical resistance first decreases linearly with temperature and then begins to decline sharply near 92 K and reaches zero near 89 K. In both samples, the T_{con} (onset

transition temperature) was about 92 K and T_{coff} (offset transition temperature)(T_c) at which the electric resistance becomes zero was about 89 K. There is no visible effect of PVA addition on T_c. The distribution of T_c values in the large samples prepared from the slurry with (a) 0 wt% and (b) 1 wt% PVA concentration shows in Fig. 5 (a) and (b), respectively. These results indicated that the whole of both samples would be superconductors under 85 K. Average T_c of samples prepared from the slurry with (a) 0 wt% and (b) 1 wt% PVA was 87.6±2 K and 88.6±2 K, respectively.

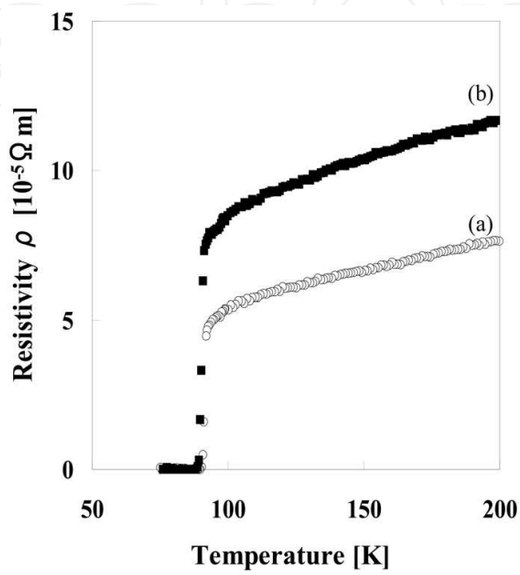

Fig. 4. Dependence of resistivity on temperature. The samples were prepared from the slurry with various PVA concentrations: (a) 0 and (b) 1 wt%.

The difference of average T_c for both samples was small within 1 K. The average T_c did not depend on the PVA concentration, which was in the range between 0 and 5 wt%, and the average T_c of all samples was 88.3±3 K.

89.5 K	86.2 K	86.3 K	
	88.3 K	88.5 K	
	88.3 K		
85.4 K			88.5 K

(a)

88.4 K	89.4 K	87.5 K	88.4 K
	88.0 K	89.5 K	
87.0 K	87.5 K	89.5 K	
		89.0 K	90.0 K

(b)

Fig. 5. The distribution of Tc values in the samples prepared from the slurry with (a) 0 wt% and (b) 1 wt% PVA concentration.

Figure 6 shows the dependence of current density on the magnetic flux density measured at 77K for the samples prepared from the slurry with the PVA concentrations of (a) 0 wt% and

(b) 1 wt%. The samples used were the same as those in Fig. 4. The current density of the sample prepared from the slurry with 1 wt% PVA is larger than that of the sample without PVA for the magnetic field range between -1.0 and +1.0 T. It can be seen that with the addition of PVA, the critical current density (***Jc***) increased from 370 to 713 A/cm^2. This ***Jc*** of 713 A/cm^2 was about 35% of the reported ***Jc*** (about 2000 A/cm^2) of the$YBa_2Cu_3O_{7-x}$ polycrystalline sample produced by the Bridgman method. The distributions of ***Jc*** values, which were observed at 77 K at 0.018T, on the large samples used in Fig. 6(a)0% and (b)1% are shown in Fig. 7(a) and (b), respectively. From Fig. 7(a), ***Jc*** values of the sample prepared without PVA were distributed in the range from 253 to 443 A/cm^2, and that the average ***Jc*** of this sample was 340±70 A/cm^2 (except maximum and minimum ***Jc***). From Fig. 7(b), ***Jc*** values of the sample prepared from the slurry containing 1% PVA were distributed in the range from 587 to 890 A/cm^2, and that the average ***Jc*** of this sample was 755±135 A/cm^2 (except maximum and minimum ***Jc***).

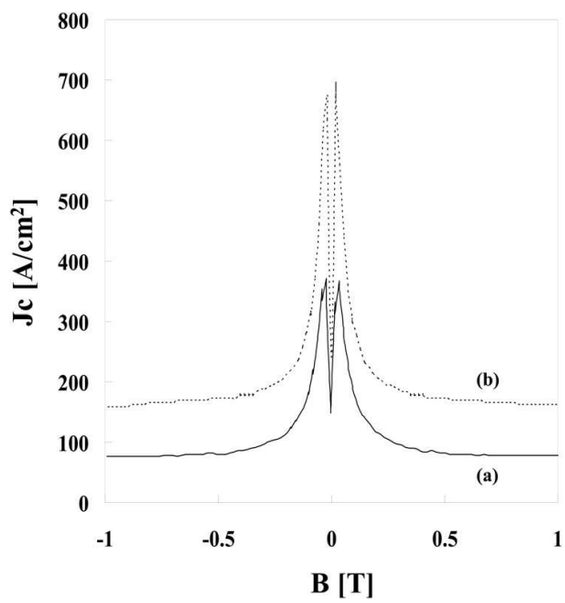

Fig. 6. Dependence of current density on magnetic flux density. The samples were prepared from the slurry with various PVA concentrations: (a) 0 and (b) 1 wt%. Measurement was performed at 77 K.

Comparing with Fig. 7(a) and (b), it is found that the average ***Jc*** value of the sample prepared from the slurry containing 1 wt% PVA was about two times larger than that of the sample without PVA. This fact can be explained by the difference of the density. The average density of the sample without PVA and with 1 wt% PVA was 4.6±0.3 g/cm^3 and 5.4±0.4 g/cm^3, respectively. Since our samples consist of polycrystalline samples, the number of the superconducting path in the sample increases with increase in the density of the sample so that ***Jc*** value of the sample prepared with 1 wt% PVA became larger than that of the sample without PVA. In our studies, over 1 wt% PVA, Jc values decreased with increases in PVA concentration. The reason for this decrease of Jc was thought that when the amount of PVA included in the sample increased, after firing, the amount of the residual carbon and related impurities, which exist along the grain boundary, increased so that the decrease of ***Jc*** was observed. In our studies, the optimum PVA concentration was 1 wt%.

Figure 8 is the photograph that Meissner effect is observed by the sample used in Fig. 7(b). In this picture, sample was cooled at 77 K with liquid nitrogen. This figure indicates that our sample made by the plastic forming method was a superconducting material.

			270
370	334		
	366	443	357
	345		253

(a)

730		740	880
	887	713	751
890	670	790	
		630	587

(b)

Fig. 7. The distribution of Jc values in the samples prepared from the slurry with (a) 0 wt% and (b) 1 wt% PVA concentration. Jc measurement was done at 0.018 T.

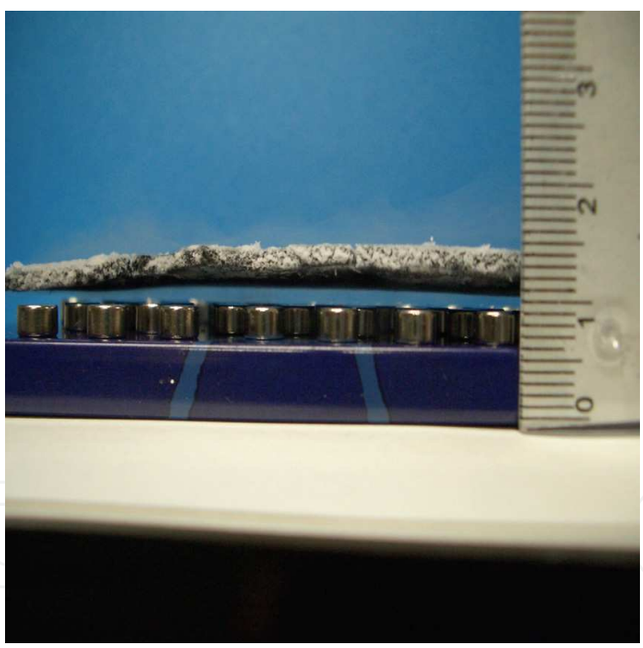

Fig. 8. The photograph of Meisser effect of the sample used in Fig. 7(b)

3. Improvement of the superconducting properties

The maximum average ***Jc*** observed in this study was about 755 A/cm^2, which is much smaller than the reported maximum ***Jc*** of the bulk $YBa_2Cu_3O_{7-x}$ sample (>10^4 A/cm^2). The main reasons why ***Jc*** is much smaller than the reported value are as follows:

1. The density of samples prepared from the slurry containing 1 wt% PVA (5.4±0.4 g/cm^3) is about 86 % of the theoretical density (d=6.36 g/cm^3).

2. The sample is a polycrystal in which the degree of orientation to the c-axis is low.
3. Non-superconducting materials exist among grain boundaries.
4. The degree of oxygen deficiency is large.
5. The degree of crystallinity of used $YBa_2Cu_3O_{7-x}$ powder/particle was of no high quality.

We tried to improve the superconducting properties of our samples.

(1) Oxygen annealing

It has been well known that the oxygen defect strongly affects the crystal structure and the superconducting properties of HTS. Therefore, we tried to improve the superconducting properties of samples by the oxygen annealing.

Figure 9 shows the dependence of current density on magnetic flux density of (a) non-heat-treated sample and (b) heat treated sample[11]. Heat treatment was done at 773 K, 10 h, under oxygen gas flow condition. It is found that by the heat treatment in an oxygen atmosphere, the current density increased about three or four times more than that of non-heat-treated sample and especially ***Jc*** value at 0.018 T was about 1500 A/cm² and this value was about 70% of the reported value for under doped $YBa_2Cu_3O_{7-x}$ prepared with Bridgman method[12]. And this fact implies that the superconducting properties can be improved by the heat treatment in the oxygen atmosphere.

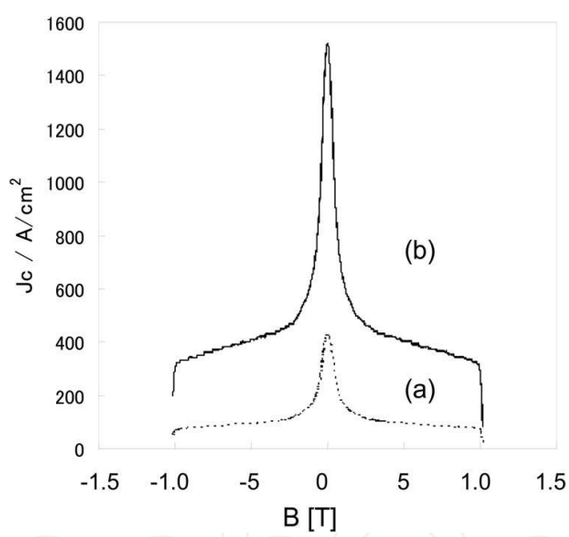

Fig. 9. The dependence of current density on magnetic flux density of (a) non-heat-treated sample and (b) heat treated sample. Heat treatment was done at 773 K, 10 h, under oxygen gas atmosphere.

(2) Changing of $YBa_2Cu_3O_{7-x}$ powder/particles

In general, the degree of crystallinity of the $YBa_2Cu_3O_{7-x}$ powder/particles prepared with conventional sintering method was of poorer quality than that prepared with other methods such as MPMG method, Bridgman method, etc, so that near 0 T, superconducting properties of $YBa_2Cu_3O_{7-x}$ samples made by conventional sintering method became of less quality inhomogeneos than those prepared with other methods. Changing of $YBa_2Cu_3O_{7-x}$ powder/particles prepared with conventional sintering method to $YBa_2Cu_3O_{7-x}$ powder/particles prepared with MPMG method, we tried to improve superconducting properties.

Figure 10 shows the dependence of current density on magnetic flux density of (a) the sample prepared with $YBa_2Cu_3O_{7-x}$ powder/particles made by convenience sintering

method and (b) the sample prepared with powder/particles made by MPMG method [2]. ***Jc*** value and ***Tc*** of $YBa_2Cu_3O_{7-x}$ powder/particles made by convenience sintering method was about 700 A/cm² and 89 K, respectively. On the other hand, ***Jc*** value and ***Tc*** of $YBa_2Cu_3O_{7-x}$ powder/particles made by MPMG method was about 2000 A/cm² and 89 K, respectively. From results in Fig. 9, ***Jc*** values of samples prepared with $YBa_2Cu_3O_{7-x}$ powder/particles made by (a) convenience sintering method and (b) MPMG method were about 900 and about 2900 A/cm², respectively. It is also found that ***Jc*** value of the sample prepared with powder/particles made by MPMG method is about three times larger than that of the sample prepared with powder/particles made by convenience sintering method. And it is found that using powder/particles made by MPMG method, the superconducting properties near 0 T were improved. This fact indicates that if the $YBa_2Cu_3O_{7-x}$ powder/particle, which has larger ***Jc*** value, will be used, the ***Jc*** value of the sample made by plastic forming will be larger than those of our reported samples.

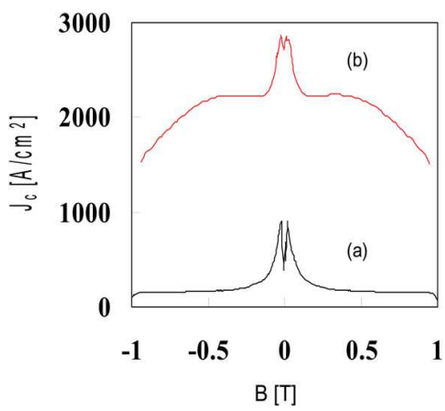

Fig. 10. The dependence of current density on magnetic flux density. Sample (a) was prepared with $YBa_2Cu_3O7_{-x}$ powder made by conventional sintering method. Sample (b) was prepared with $YBa_2Cu_3O7_{-x}$ powder made by MPMQ method.

4. Conclusion

In this work, we have described that large $YBa_2Cu_3O_{7-x}$ superconductor samples can be easily prepared with the plastic forming which is the preparation method for large scale ceramics samples with simple, easy and reproductive processes. Used slurry was prepared by mixing $YBa_2Cu_3O_{7-x}$ particles which were prepared with the sintering method, the inorganic binder and polyvinyl alcohol (PVA). In this method, fine $YBa_2Cu_3(OH)_x$ colloid particles (average particle diameter : 380±70 nm) prepared with the sol-gel method was used as inorganic binder and polyvinyl alcohol (PVA) was used as protective colloid and also acted as flocculant (aggregation agent). Adding a small amount of PVA into the slurry, the clack generation was reduced and so that large scale bulk $YBa_2Cu_3O_{7-x}$ superconductor (about 100 mm x 100 mm x 2 mm) could be produced. The sample became superconducting at 88.3±3 K and had the average ***Jc*** of 755±135 A/cm².

To improve superconducting properties, we changed the $YBa_2Cu_3O_{7-x}$ powder/particles prepared with conventional sintering method to $YBa_2Cu_3O_{7-x}$ powder/particles prepared with MPMG method. So that the samples became superconducting at 91.5±0.5 K and had average critical current density 2900±200 A/cm² (at 77 K under H=0.018 T). This result indicates that superconducting properties, especially ***Jc*** value, of samples made with plastic

forming are determined by those of used $YBa_2Cu_3O_{7-x}$ powder/particles. Therefore, superconducting properties of sample prepared with plastic forming will be improved by both optimizations of $YBa_2Cu_3O_{7-x}$ powder/particles and $YBa_2Cu_3(OH)_x$ colloid particles.

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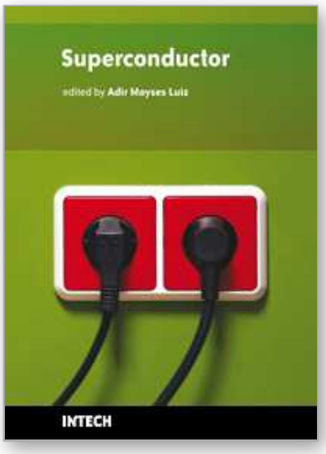

Superconductor

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This book contains a collection of works intended to study theoretical and experimental aspects of superconductivity. Here you will find interesting reports on low-Tc superconductors (materials with Tc< 30 K), as well as a great number of researches on high-Tc superconductors (materials with Tc> 30 K). Certainly this book will be useful to encourage further experimental and theoretical researches in superconducting materials.

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