

Effect of orientation of *c*-axis on Ba₄CuPt₂O₉ compounds of fluorine-doped YBa₂Cu₃O_x superconductors

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An experimental study has been carried out to investigate a synergistic effect of Ba₄CuPt₂O₉ compounds on the critical current density to fluorine-doped YBCO superconductors. The Ba₄CuPt₂O₉ compounds were synthesized by a solid state reaction. It was found that the synthesis temperature of the Ba₄CuPt₂O₉ compounds was over 800 °C, which was higher than that of a paper ever reported. In addition, the influence of the Ba₄CuPt₂O₉ compounds on the critical current density to the YBCO superconductors has been investigated to use two types of Ba₄CuPt₂O₉ compound. One is not heat-treated, i.e., source materials, and the other is heat-treated at 950 °C. It was found that the former affected the orientation of *c*-axes, but the latter did not have an influence on the orientation to the *c*-axes, and molested the superconductivity to the samples quenched at temperatures above 850 °C. © 1999 Kluwer Academic Publishers

1. Introduction

The critical current density in high-*T_c* superconductors is not enough to apply to the power applications, and is also theoretically expressed as a balance of the Lorentz force and pinning force [1]. The pinning centers in high-*T_c* superconductors have not been elucidated completely. However, the dominant pinning center in YB₂Cu₃O_x (YBCO) superconductors has been well known as Y₂BaCuO₅ particles [2–4]. It has been reported that the critical current density in the YBCO superconductor increases with increasing a volume fraction and with decreasing the size of Y₂BaCuO₅ particle, that is, the following conditions are necessary for the YB₂Cu₃O_x superconductors to obtain high critical current density; the certain value of volume fraction of the Y₂BaCuO₅ particles is included in the volume, and the size of the Y₂BaCuO₅ particle is desirable for the pinning center as fine as possible [5].

Concerning the size of Y₂BaCuO₅ particles in the YBCO superconductor, it has been reported that a small amount of platinum doped YBCO superconductors attained a high critical current density at high temperatures and/or high magnetic fields [6, 7]. This was caused by decreasing size of the Y₂BaCuO₅ particles in the YBCO superconductor [5, 7]. In addition to the above fact, the platinum doped to the YBCO superconductors forms a Ba₄CuPt₂O₉ compound in the synthesis process of YBCO superconductors. The Ba₄CuPt₂O₉ compounds are especially related to decreasing the size of Y₂BaCuO₅ particles [6, 8]. The present authors syn-

thesized YBCO superconductors with fine Y₂BaCuO₅ particles at lower synthesis temperature than that of the QMG (Quench and Melt Growth) method by doping fluorine [9, 10]. Therefore, we investigate a synergistic effect of the Ba₄CuPt₂O₉ compounds to the fluorine-doped superconductors on the critical current density.

For the purpose, we prepared and used two types of Ba₄CuPt₂O₉ compound such as: additivity 1, (this is not heat-treated), and additivity 2, (this was heat-treated at 950 °C, and Ba₄CuPt₂O₉ compound was completed.). The applied techniques were differential thermal analysis (DTA), X-ray diffractometry (XRD), and vibrating system for magnetization (VSM).

2. Experimental

The nominal YBa₂Cu₃F_{0.4}O_x compositions used in this study were prepared from YBa₂Cu₃O_x and YBa₂Cu₃F₄O_x powders [11]. YBa₂Cu₃O_x powder was synthesized from Y₂O₃, BaCO₃ and CuO. YBa₂Cu₃F₄O_x powder was synthesized from Y₂O₃, BaF₂ and CuO. The two master powders, YBa₂Cu₃O_x and YBa₂Cu₃F₄O_x, were calcined at 900 °C for 8 h in air. They mixed to yield YBa₂Cu₃F_{0.4}O_x, which were added a small amount of platinum, and were then quenched at different temperatures. The reason why we used molar ratio of 0.4 mol fluorine, the samples exhibited larger magnetic hysteresis curves with this molar ratio than others, as in metallic superconductors, with strong pinning strength [10]. The fluorines included in

the above nominal composition worked as a catalyst during synthesizing YBCO superconductors, and they evaporated into air while the YBCO were being cooled to room temperature [12].

BaCO₃, CuO, and PtO₂ powders of 99.99% purity each were prepared for a source material of Ba₄CuPt₂O₉ compound.

DTA was performed on a source material at temperatures up to 1000 °C in air. The experimental conditions were as follows: sampling rate 1.0 s, increasing temperature rate 10 °C/min, and temperature was measured using a platinum thermocouple. XRD measurements were carried out in order to obtain the informations of the Ba₄CuPt₂O₉ compound and the formation of YBCO superconductors. The critical current densities were estimated from a wide of the magnetization curve in a magnetic field up to 1 T using a VSM equipment at 77 K. Microstructural observation is done by using an optical microscope.

3. Results and discussion

3.1. Comparison of DTA curves in YBa₂Cu₃F_{0.4}O_x and YBa₂Cu₃O_x

We shall compare a DTA result of a fluorine-doped superconductor (YBa₂Cu₃F_{0.4}O_x) with that of an undoped superconductor (YBa₂Cu₃O_x), and we explain why we used the YBa₂Cu₃F_{0.4}O_x. Fig. 1 shows results of DTA for the above YBa₂Cu₃F_{0.4}O_x and YBa₂Cu₃O_x. The dotted and solid lines indicate the DTA results for the YBa₂Cu₃O_x and YBa₂Cu₃F_{0.4}O_x, respectively. Concerning to the YBa₂Cu₃F_{0.4}O_x, endothermic peaks can be observed four peaks at temperatures above 800 °C. On the other hand, DTA result for YBa₂Cu₃O_x can be observed three peaks at temperatures above 800 °C. It is certain that the temperatures at the largest endothermic peaks of the two DTA curves differ obviously. The endothermic peaks are generally interpreted

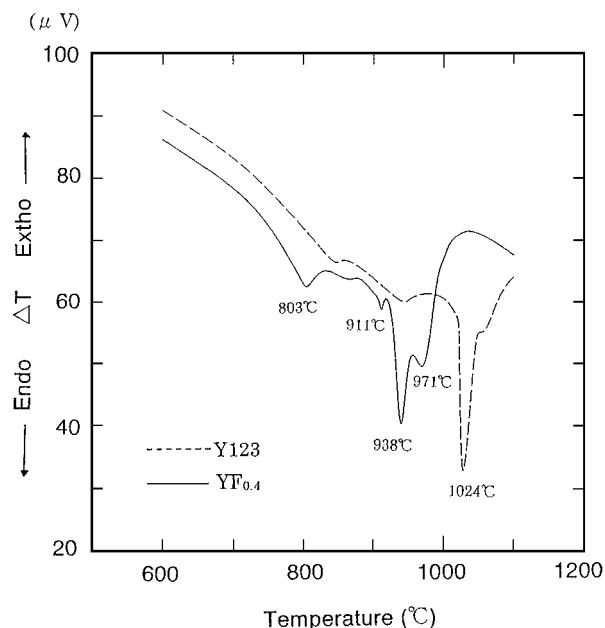


Figure 1 DTA results of YBa₂Cu₃F_{0.4}O_x and YBa₂Cu₃O_x. The largest endothermic peak in YBa₂Cu₃F_{0.4}O_x exists at temperature of 938 °C, and for YBa₂Cu₃O_x the largest peak appears at temperature of 1024 °C. This difference of temperatures is caused by an effect of fluorine as a flux.

as transitions of melting and/or crystallization. If we assume that the largest endothermic peaks reflect the transition of melting in the powder samples, it seems that power sample partly melts at the temperature of the largest peak. If so, the melting temperature will decrease by about 100 °C in comparison with that of the YBa₂Cu₃O_x sample. It is found that the fluorine added to the samples works as a kind of flux. It is useful to decrease a synthesis temperature of YBCO superconductors for their applications. Therefore, we used YBa₂Cu₃F_{0.4}O_x, in consideration with the DTA result.

A DTA result for a small amount of PtO₂ added in YBCO superconductor has been reported [6]. The temperatures of endothermic peaks in the DTA curve are nearly equal to that of the above DTA result of YBa₂Cu₃O_x. The endothermic peaks in the above paper were also explained as the synthesis temperatures of e1, p1 and m1, here e1: YBa₂Cu₃O_{7-x} + BaCuO₂ + CuO → liquid, p1: YBa₂Cu₃O_{7-x} + CuO → Y₂BaCuO₅ + liquid, and m1: YBa₂Cu₃O_{7-x} → Y₂BaCuO₅ + liquid. If there endothermic peaks correspond similarly to those of YBa₂Cu₃F_{0.4}O_x, it will be expected that decrease of synthesis temperatures contributes to the applications in high-*T_c* superconductors.

3.2. Synthesis temperature of Ba₄CuPt₂O₉ compound

We are interested in the synthesis temperature of Ba₄CuPt₂O₉ compound. In a Ref. [7], the synthesis temperature of Ba₄CuPt₂O₉ compound was described as a temperature of 700 °C. First of all, we checked the synthesis temperature of a Ba₄CuPt₂O₉ compound using XRD and DTA. Fig. 2 shows X-ray diffraction patterns of source materials of Ba₄CuPt₂O₉ compound quenched at different temperatures. Here, the quenched temperatures were from 700 to 950 °C at intervals of 50 °C. An X-ray diffraction pattern shown in a Ref. [13]

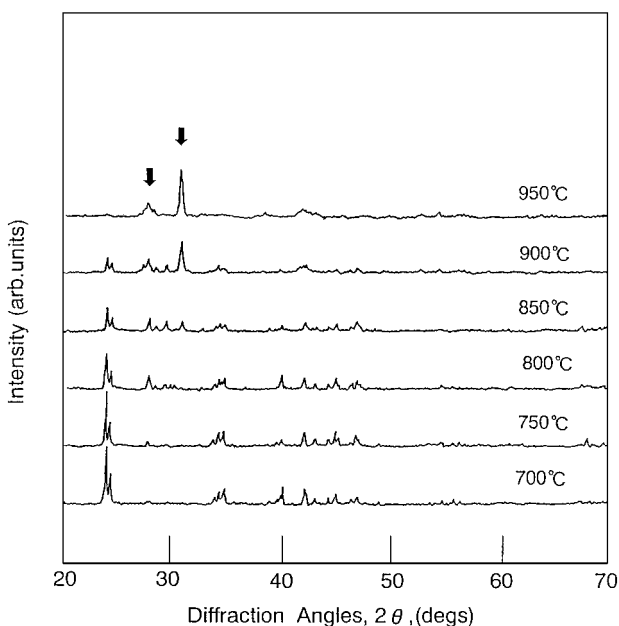


Figure 2 X-ray diffraction patterns for source materials of Ba₄CuPt₂O₉ compound quenched at different temperatures. Synthesis temperature of Ba₄CuPt₂O₉ compound can be confirmed at temperatures above 750 °C (see arrows). This temperature differs from that of Ref. [13].

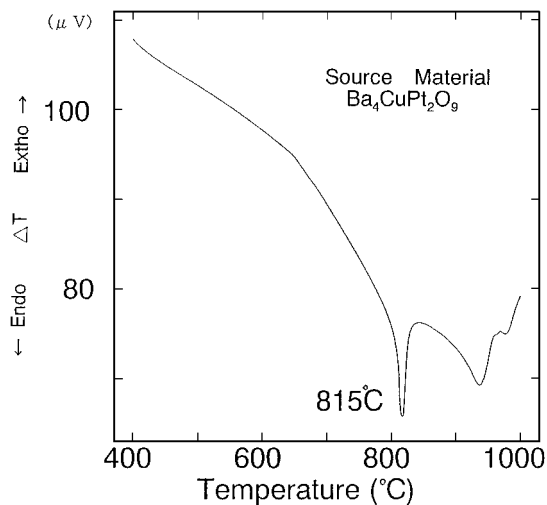


Figure 3 A DTA result at temperatures up to 1000 °C for additivity 1. A large endothermic peak appears at 815 °C, if this is a synthesis temperature, this differs from a synthesis temperature ever reported.

does not correspond to our result. The same pattern shown in the Ref. [13] is obtained at a temperature of 950 °C. For two large diffraction peaks at 27.4° and 30.6° (see arrows), even the largest diffraction peak at 30.6° disappears at temperatures below 800 °C. Concerning to the diffraction peaks at 27.4°, it can be observed at a temperature of 750 °C, but its signal is much smaller than that of the other phases. Hence, it is found that Ba₄CuPt₂O₉ compounds are not easily synthesized at temperatures below 750 °C. It is necessary for synthesis of Ba₄CuPt₂O₉ compounds to synthesize them at temperatures above 800 °C. It is expected that the synthesis of Ba₄CuPt₂O₉ compounds is reasonably reflected to the DTA result. The source materials of Ba₄CuPt₂O₉ compound, additivity 1, were measured with DTA at temperatures up to 1000 °C. The result is shown in Fig. 3. The DTA curve decreased with increasing temperature, and the endothermic peak appeared at a temperature of 815 °C. This temperature mostly correspond to the temperature appeared Ba₄CuPt₂O₉ compound for X-ray diffraction measurements shown in Fig. 2. However, it is not clear that where the onset temperature of the endothermic peak in Fig. 3 is at a temperature nearby 650 or 800 °C. Since there is no peak of Ba₄CuPt₂O₉ compounds for a sample quenched at 700 °C in Fig. 2, the onset temperature will be considered at a temperature of nearby 800 °C.

3.3. Addition of two types of additivity to YBCO

Two types of source materials of Ba₄CuPt₂O₉ compound, addivities 1 and 2, were added to YBa₂Cu₃F_{0.4}O_x in order to investigate a synergistic effect on the critical current density. First of all, an optimum amount of additivity 1 for the YBa₂Cu₃F_{0.4}O_x were decided. The additivity 1 added to YBa₂Cu₃F_{0.4}O_x were carried out in weight percentages of 0.1, 0.5, 0.7, 1.0, and 1.5. Fig. 4 shows X-ray diffraction patterns for the above samples mentioned. It is found that diffraction peaks oriented to *c*-axis are observable in comparison with a standard sample [14]. Although position of the

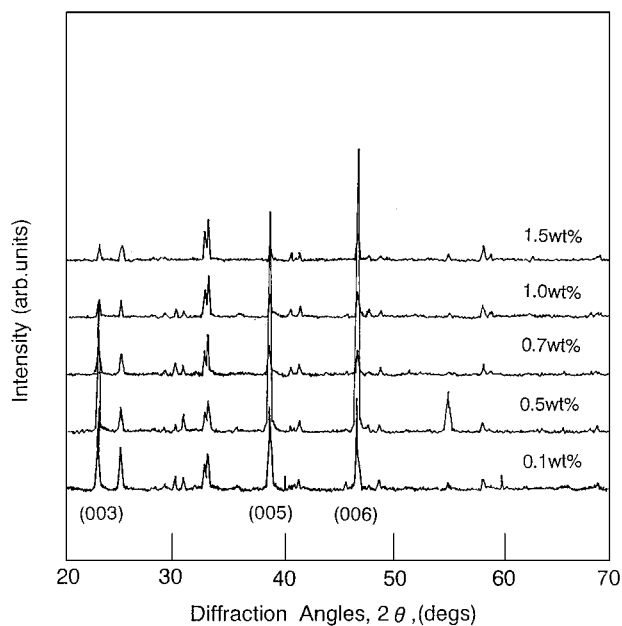


Figure 4 X-ray diffraction patterns for samples with different amounts of additivity 1. Diffraction peaks oriented to *c*-axis are observable in comparison with a standard sample.

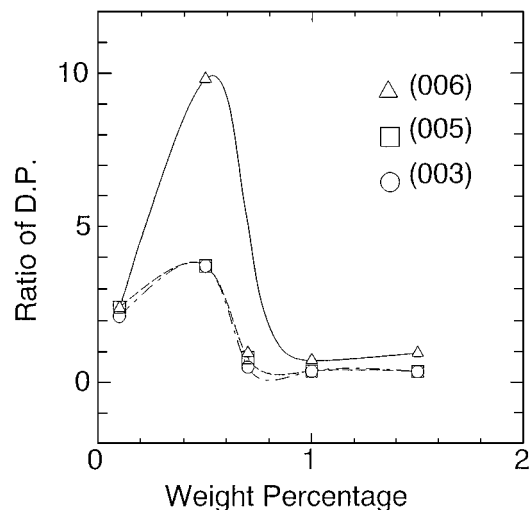


Figure 5 A dependence of addition of additivity 1. Longitudinal axis shows a ratio of diffraction peak at 32° to another peaks oriented to *c*-axes. Signals of (006) increase evidently up to 0.5 wt %.

maximum diffraction peak of the standard sample appeared in the vicinity of 32°, diffraction peaks oriented to the *c*-axis, (003), (005), and (006), are larger than that of 32°. We shall compare the diffraction peak at 32° with those of the oriented to the *c*-axis for all samples shown in Fig. 4. Longitudinal and horizontal axes in Fig. 5 show ratios of a maximum diffraction peak at 32° to those peaks oriented to the *c*-axes, and weight percentage of additivity 1, respectively. In accordance with increasing in the weight percentages of additivity 1, the ratios of a diffraction peak at 32° to the diffraction peaks oriented to *c*-axis increased evidently up to 0.5 wt %. There were hardly changes of the ratios of the maximum diffraction peak at 32° to the diffraction peaks oriented to *c*-axis for the other weight percentages. Therefore, weight percentage of additivity 1 for samples was used 0.5 wt % in subsequent experiments.

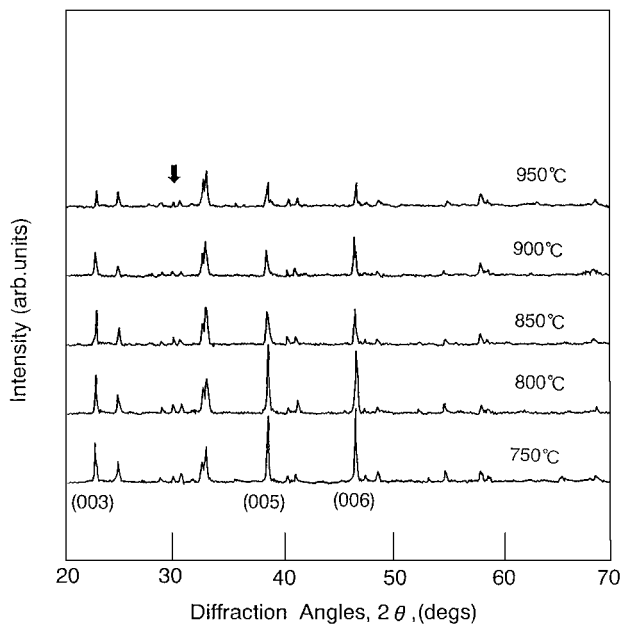


Figure 6 X-ray diffraction patterns for samples added additivity 1. The samples are quenched at different temperatures. Diffraction peaks oriented to c -axes are fairly observable.

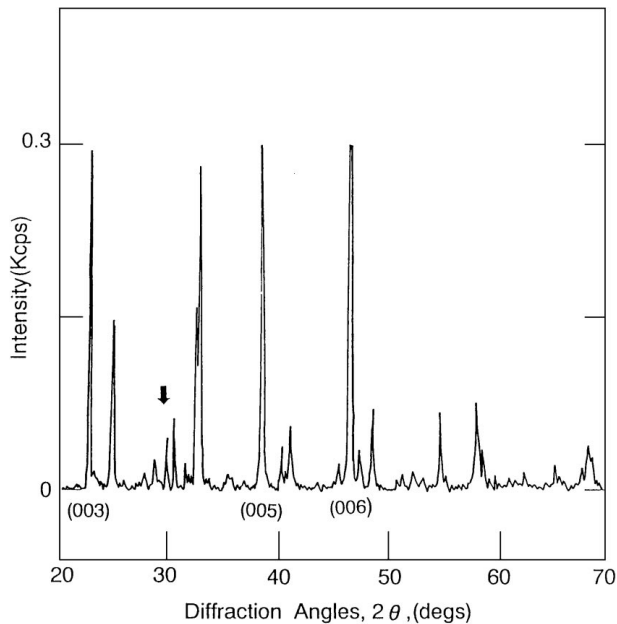


Figure 7 X-ray diffraction pattern for a sample quenched at temperature of 750 °C. It seems that diffraction peak at 30.5° agrees with that of Y_2BaCuO_5 normal particles because the occurrence of $Ba_4CuPt_2O_9$ phases is not at temperature of 750 °C in Fig. 4.

It can be believed that additivity 1 has something to do with the orientation of c -axes. So, if the preparation condition of additivity 1 is changed, it is expected that the influences to the orientation may be clear by changing the preparation condition of the additivity. Therefore, we prepared additivity 2 (heat-treated at 950 °C) for the above investigation. Fig. 6 shows X-ray diffraction patterns for samples added additivity 1, and quenched at different temperatures. Diffraction peaks oriented to c -axes are fairly observable, and these are remarkable diffraction patterns at quenching temperatures of 750 and 800 °C. The diffraction peaks oriented to the c -axes are larger than the diffraction peak at 32°. A small diffraction peak at 30.5° can be observed (see arrow). There is a doubt for the diffraction peak whether it is a diffraction peak of $Ba_4CuPt_2O_9$ compound because the diffraction peak is put its diffraction angle on that of Y_2BaCuO_5 particles. Hence, the X-ray diffraction pattern quenched at a temperature 750 °C is magnified in the sensitivity of Y -axis to 0.3 (kcps) in maximum as shown in Fig. 7. It seems that the diffraction peak at 30.5° agrees with that of Y_2BaCuO_5 particles because the occurrence of $Ba_4CuPt_2O_9$ phases is not at temperature of 750 °C in Fig. 4. Let us compare diffraction peaks oriented to c -axes with that at 32°. The result is shown in Fig. 8. Two peaks of (005), and (006) are about two times larger than that at 32° up to 800 °C, but the ratios of diffraction peaks decrease with increasing temperatures quenched. It is seemed that the additivity 1 itself may be decomposed or diffused at temperatures above 750 °C, and in the process of decomposing there may be a mechanism to be oriented to c -axis for the diffraction peaks. If so, it is expect that shapes of X-ray diffraction patterns will change for change of condition in the additivity. So, we used additivity 2 for the above purpose, since the $Ba_4CuPt_2O_9$ compound in Fig. 4 were stabilized chemically. Fig. 8 shows a

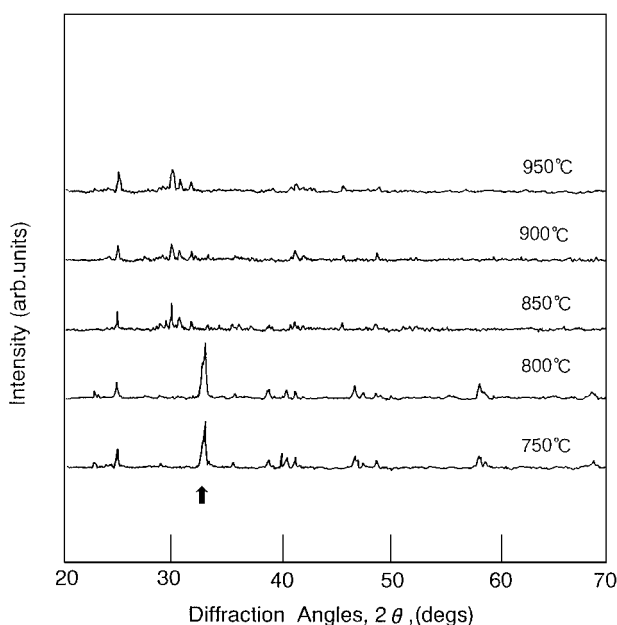


Figure 8 X-ray diffraction patterns for samples with additivity 2 quenched at different temperatures. There are diffraction peaks at 32° at temperatures up to 800 °C, but they are not at temperatures above 850 °C.

result of X-ray diffraction patterns quenched at different temperatures for samples with additivity 2. We can observe that the diffraction peak at 32° exists at temperatures up to 800 °C, but it is not at temperatures above 850 °C. It seems that the growth of superconducting phases may be opposed by an addition of the additivity 2. That is, the additivity 2, which has been already accomplished as a $Ba_4CuPt_2O_9$ compound, worsened both the orientation of the c -axes and the superconductivity of the samples sintered at temperatures above 850 °C. It is considered that additivity 1 has something to do with elements of the $YBa_2Cu_3F_{0.4}O_x$ in

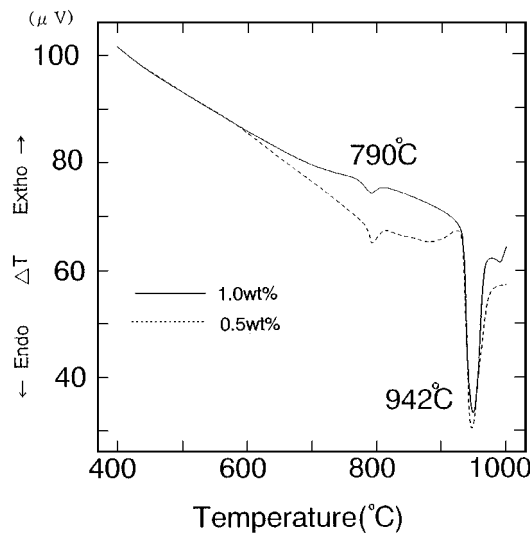


Figure 9 DTA result for samples with different amounts of additivity 2. Endothermic peaks are observed at temperatures 790 and 942 °C. It is considered that these endothermic peaks may be act by the $\text{YBa}_2\text{Cu}_3\text{F}_{0.4}\text{O}_x$ because these peaks correspond mostly to the endothermic peaks of $\text{YBa}_2\text{Cu}_3\text{F}_{0.4}\text{O}_x$ in Fig. 1.

the synthesis process because the diffraction patterns are not obstructed for the additions of the additivity 1. However, since the additivity 2 is chemically stable to $\text{YBa}_2\text{Cu}_3\text{F}_{0.4}\text{O}_x$, the condition of the superconductivity may be worsened by the additivity 2. A diffraction peak at 32° decreases than the other peaks at temperatures above 850 °C. DTA measurements were, then, performed for samples with different amounts of additivity 2. The result is shown in Fig. 9. Endothermic peaks are observed at temperatures 790 and 942 °C for the samples. It is considered that these endothermic peaks may be act by the $\text{YBa}_2\text{Cu}_3\text{F}_{0.4}\text{O}_x$ because these peaks correspond mostly to the endothermic peaks of $\text{YBa}_2\text{Cu}_3\text{F}_{0.4}\text{O}_x$ in Fig. 1. That is, additivity 2 is not given thermal changes to the $\text{YBa}_2\text{Cu}_3\text{F}_{0.4}\text{O}_x$, and this is also supported that the additivity 2 is chemically stable to the $\text{YBa}_2\text{Cu}_3\text{F}_{0.4}\text{O}_x$.

3.4. The critical current density

The critical current densities, J_c s, in samples 1, 2, and 3 listed in Table I were estimated from the width of the magnetization curve measured using a VSM equipment at 77 K. The maximum value in the samples was obtained $1.07 \times 10^8 \text{ A/m}^2$ at 0.5 T. Especially, this is not an especial value, but in comparison with that of the sample not added, sample 3, the critical current density increased nearly 30% larger than that of the sample 3.

TABLE I The critical current density estimated from magnetization curves at 77 K

Samples	$J_c(\text{A/m}^2)$ (at 0.5 T and 77 K)	Size ($L \times w \times t$) (mm)
1. YBCOF0.4 (+ additivity 1)	1.07×10^8	$12 \times 3.0 \times 1.9$
2. YBCOF0.4 (+ Pt 0.3 wt %)	0.95×10^8	$8 \times 2.5 \times 1.8$
3. YBCOF0.4 (+ non)	0.87×10^8	$10 \times 4.1 \times 2.2$

It is considered that the increase of the critical current density will be caused by an orientation of the c -axis or microstructural changes. Then, microstructural observation was done for the above samples 1 and 3. The microstructural photographs are shown in Fig. 10. It is found that there are hardly changes of the microstructure for the two samples. From this result, the above supposition for the increase of the critical current density may be supported. However, these the critical current densities of the two samples are hardly changed. Since the samples used for a measurement of the critical current density were cut from the bulk samples, it is not easy for us to describe exactly the effect of the orientation of the c -axis. That is, it is not clear for the sample 1 how much volume is oriented to the c -axis. In fact, these samples included many defects, and there is a possibility that the defects work as pinning centers. If these are considered for the increase of the critical current density, the reason of the increase of the critical current density will be a very complicated matter. Since there is hardly change for the two samples on the defects and/or microstructure conditions, the orientation to the c -axis will be believed to contribute to increase the critical current density. If the effect of orientation of the c -axis on the YBCO would like to show its effect fully for increasing the critical current density, this can be confirmed in the materials of tape wires and/or thin films. Because these materials can be produced in the homogeneity than the bulk materials.

4. Conclusions

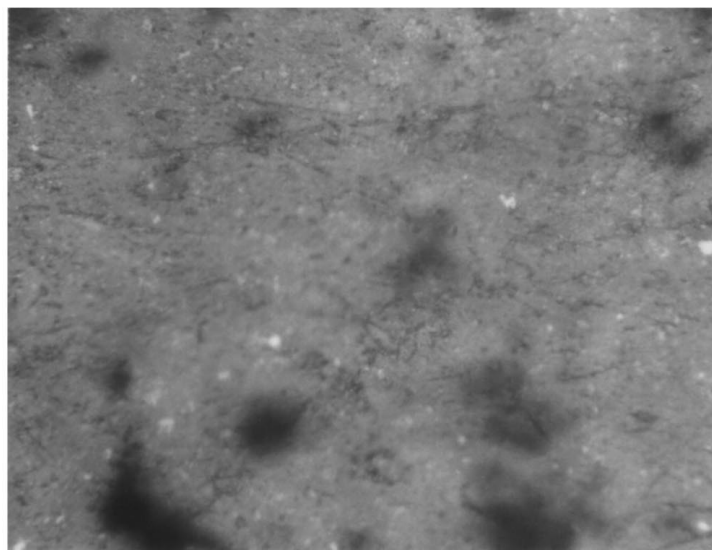
An experimental study has been carried out to investigate a synergistic effect of $\text{Ba}_4\text{CuPt}_2\text{O}_9$ compounds to fluorine-doped YBCO superconductors. The obtained results are as follows:

1. At temperatures endothermic peaks appeared in a DTA result in $\text{YBa}_2\text{Cu}_3\text{F}_{0.4}\text{O}_x$ decreased about 100 °C in comparison with that in $\text{YBa}_2\text{Cu}_3\text{O}_x$. It was found that the fluorine added into the samples works as a kind of flux.

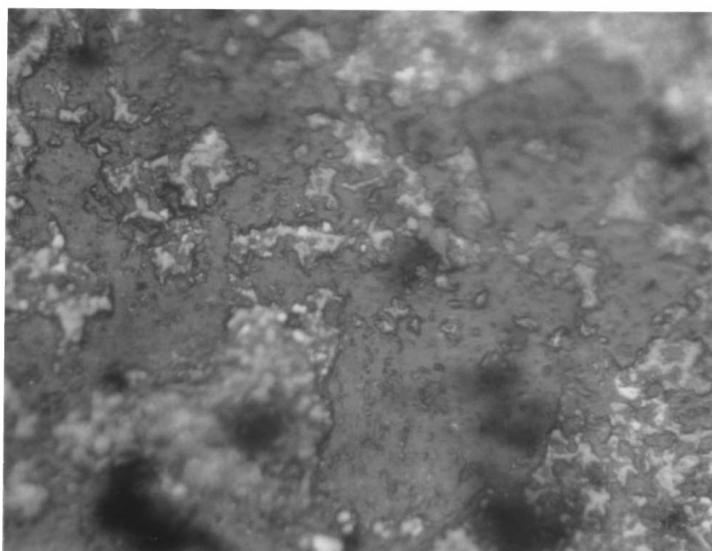
2. Synthesis temperature of $\text{Ba}_4\text{CuPt}_2\text{O}_9$ compound was measured for samples quenched at different temperatures. X-ray diffraction peaks of $\text{Ba}_4\text{CuPt}_2\text{O}_9$ compound were confirmed at temperatures above 800 °C for the second large peak, and the largest peak at $2\theta = 30.6^\circ$ disappeared at temperatures below 800 °C. It was found that the synthesis temperature of the $\text{Ba}_4\text{CuPt}_2\text{O}_9$ compound needs a synthesis temperature over 800 °C.

3. Additivity 1 influenced the orientation of the c -axes during the synthesis process, but additivity 2 did not influence the orientation of c -axes, and molested the superconductivity at temperatures above 850 °C.

4. The critical current density was obtained $1.07 \times 10^8 \text{ A/m}^2$ for a sample added additivity 1 at 77 K and 0.5 T. This value increased nearly 30% larger than that of a sample not added. Since there is hardly structural changes for the samples, it is considered that the increase of the critical current density is associated with the orientation of the c -axis.



sample 1



sample 3

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25 μ m

Figure 10 Microstructural observation for the samples 1 and 3. There are hardly changes for the two samples.

Acknowledgements

The authors would like to thank Drs. Y. Ueno and Y. Nakamura for their help with the experiments. We are also indebted to Drs. Y. Hamada and M. Kiuchi for preparation of the manuscript.

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Received 28 September 1998
and accepted 10 March 1999