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준용융법으로 제조한 Y-Ba-Cu-O 초전도체에서 CeO_2 첨가에 따른 초전도성

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Superconductivity of CeO_2-added Y-Ba-Cu-O Superconductors Prepared by Partial Melt Process

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Abstract The CeO_2-added Y-Ba-Cu-O oxides were prepared by the partial melt process involving the peritectic reaction, liquid + 2-1-1 phase → 1-2-3 phase, to investigate the effect of the dopant on microstructure and superconductivity. During the peritec reaction, all the added CeO_2 was converted to $BaCeO_3$ particles which were finely dispersed in large 1-2-3 grains. Superconducting transition temperature($T_cR=0$ point) of the partial-melted samples was as high as 90K regardless of CeO_2 content up to 5 wt%, which is owing to the separation of the second phase from the 1-2-3 superconducting phase.

요 약 CeO_2를 첨가한 Y-Ba-Cu-O 초전도체를 포정반응을 포함한 준용융법으로 제조하여 미세조직과 초전도성을 관찰하였다. 첨가한 CeO_2는 포정반응중에 $BaCeO_3$로 변화하였으며, 이 $BaCeO_3$는 방향성 성장한 1-2-3 초전도상의 기지에 미세하게 분산된다. 초전도체의 T_c는 첨가된 CeO_2함량에 관계없이 90K 이상으로 매우 높았다. 이는 준용융공정을 적용함으로서 제2상물질을 초전도상으로부터 분리할 수 있었기 때문으로 사료된다.

1. Introduction

Most of the rare earth elements(RE) except cerium and praseodymium have been known to form the 1-2-3 superconducting phase($RE_1Ba_2Cu_3O_y$) which reveals high T_c of about 90K.[1,2] These elements can be completely and partially substituted each other because of their similar valance state and ionic radius. In the case of the CeO_2-doped Y-Ba-Cu-O system, however, T_c decreased with increasing CeO_2 content, and the formation of second phase was observed,[3,4] suggesting that there is no solubility of cerium in 1-2-3 phase. The reason why cerium was not soluble in 1-2-3 phase was explained in term of the different valance state of Ce^{+4} from Y^{+3}, Ba^{+2} Cu^{+3} and Cu^{+2}. This fact can be available in designing a superconductor-nonsuperconductor composite which may improve critical current density and mechanical properties of the oxide superconductor.

In the present paper, effects of cerium oxide addition in Y-Ba-Cu-O oxide prepared by the partial melt process have been investigated. Reaction between dopant and 1-2-3 phase, characteristics of microstructure and superconductivity were observed by resistivity-temperature curve, AC magnetic susceptibility, magnetizaton hysteresis curve, x-ray diffraction(XRD) analysis and scanning electron microscopy(SEM).

2. Experimental procedure

The superconducting 1-2-3 powder used in the partial-melt process was prepared by the solid state reaction method using Y_2O_3(99.9 %), $BaCO_3$(99%) and CuO(99.9%) powders. Proportioned powders were well mixed in an alumina mortar with a pestle, calcined at 930 ℃ for 24 h in air and then furnace cooled. The calcined cakes were crushed, mixed with CeO_2 powders of 99.5% purity up to 5 wt%, pressed isostatically into pellets and then sintered at 950℃ for 24 h in air. The pellets were rapidly heated to 1050℃, held for 0.5 h, cooled to 1000℃ at a rate of 50℃/h, cooled again to 980℃ at 3℃/h and then held for 10 h. At this stage, textured 1-2-3 crystals were formed by the peritectic reaction of liquid phase and $Y_2Ba_1Cu_1O_5$(2-1-1 phase). In order to transform the tetragonal 1-2-3 phase to orthorhombic one, the pellets were cooled slowly down to 450℃, held for 24h and then aircooled.

Phases formed after calcination, sintering and partial melt process were identified by powder X-ray diffraction using CuKα radiation. Microstructures were investigated for the etched surface of samples by an optical polarized microscopy and scanning electron microscopy energy dispersive X-ray analysis(SEM EDX).

The zero resistance temperature of samples was measured from the resistance-temperature(R-T) curve using a four-probe method. The magnetization hysteresis curve at 77K from 0 to 2 T was estimated using commercial superconducting quantum interference devices. A sample of dimensions 3×3×5mm was used for the measurement.

3. Results and discussion

Temperature-resistiving carves of ($Y_1Ba_2Cu_3O_y+xCeO_2$, 0<x<5wt%) by the partial melt process are shown in Fig. 1. T_c of the partially melted sample process was not influenced by the CeO_2 addition. The T_c is nearly constant regardless of CeO_2 content. All the samples showed T_c above 90K which is a higher value than those of the solid-state reacted samples with CeO_2 where T_c decreased gradually with increasing CeO_2 content from 91K of the unadded sample to 83K of $Y_1Ce_{0.5}Ba_2Cu_3O_y$.[5] The difference of T_c between our sample and the solid-statereacted sample appears to be due to the different thermal treatment and their resulting microstructure.

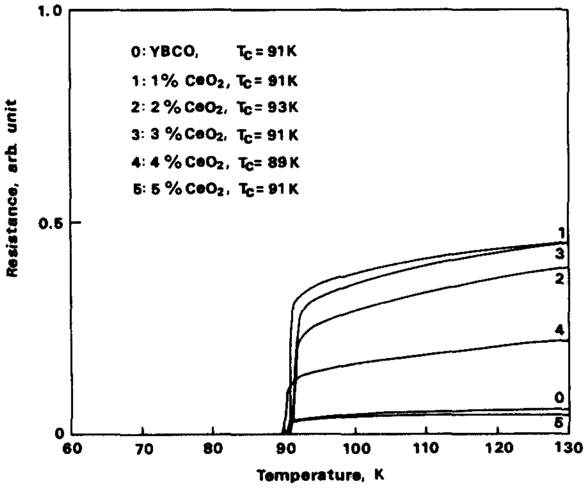

Fig. 1. Temperature-resistivity curves of unadded and CeO_2-added Y-Ba-Cu-O superconductors prepared by partial-melt process.

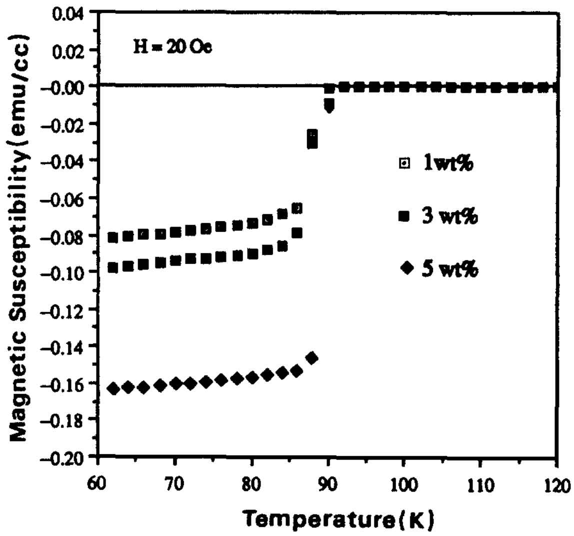

Fig. 2. AC magnetic susceptibility vs. temperature of the CeO-added Y-Ba-Cu-O oxides prepared by partial-melt process.

The AC magnetic susceptibility versus temperature of the CeO_2- added sample is shown in Fig. 2. In spite of the decrease in volume fraction of the superconducting phase, all the samples exhibit similar superconducting transition temperature. This result is consistent with the T data of Fig. 1.

The magnetic hysteresis loops for the CeO_2-added samples are presented in Fig. 3. The intergranular current density(J) can be determined from the M-H curve using the Bean model,[6)]

$$J_c = 30\triangle M/d,$$

where $\triangle M$ is the magnetization difference for increasing and decreasing magnetic fields and d is the average grain size of a sample. From the M-H curves, we could see that the intergranular J_c slightly decreased with increasing CeO_2 content. The Bean model is based on the assumption that all the material factors such as phase homogeniety are uniform. Beacuse the microstructure of our sample is not homogenious, the model could not be directly applied to the samples. Details of the microstructure charactristics will be discussed. The inhomogeniety of the material factors can be affected on the intergranular J_c because the Y-Ba-Cu-O oxide has a anisotropic superconducting properties with crystal orientation.[7)] For precise measurement of the flux pinning, the investigation for the grain aligned sample with the same crystallographic orentation is needed.

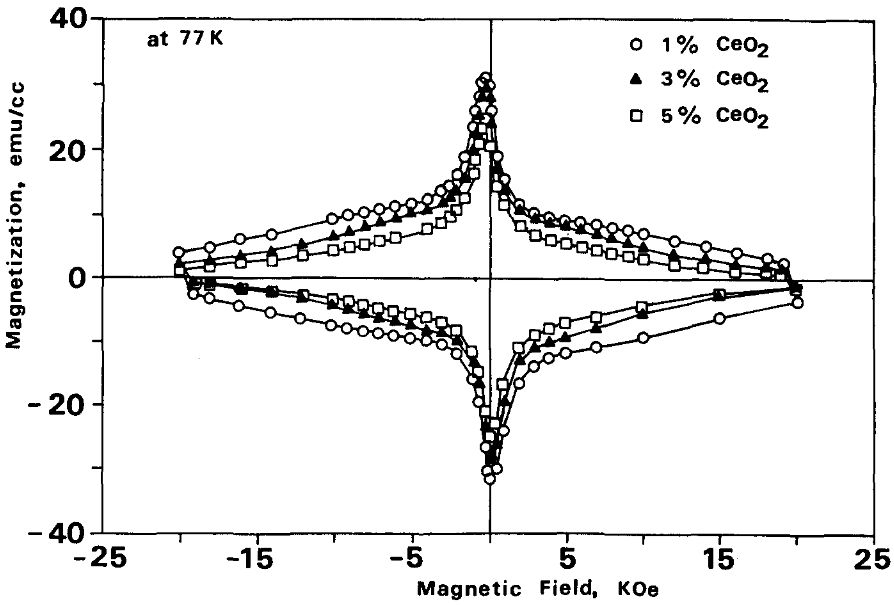

Fig. 3. The magnetic hysteresis loops of the CeO_2-added Y-Ba-Cu-O oxides prepared by partial-melt process.

The powder XRD patterns of the partial-melted sample were illustrated in Fig. 4. The pattern of unadded sample consists of orthorhombic 1-2-3 peaks. With the 1-2-3 peaks, the $BaCeO_3$ peaks are observed in the CeO_2-added samples, and the relative fraction of this phase increased with increasing CeO_2 content. In our previous report, the orthorhombic-to-tetragonal phase transition was reported in the solid-statereacted Y-Ba-Cu-O oxide with CeO_2.[5)] But the phase change was not observed in the partial-melted sample up to 5 wt% of CeO_2.

An optical polarized microstructures of partial melted samples are shown in Fig. 5. In case

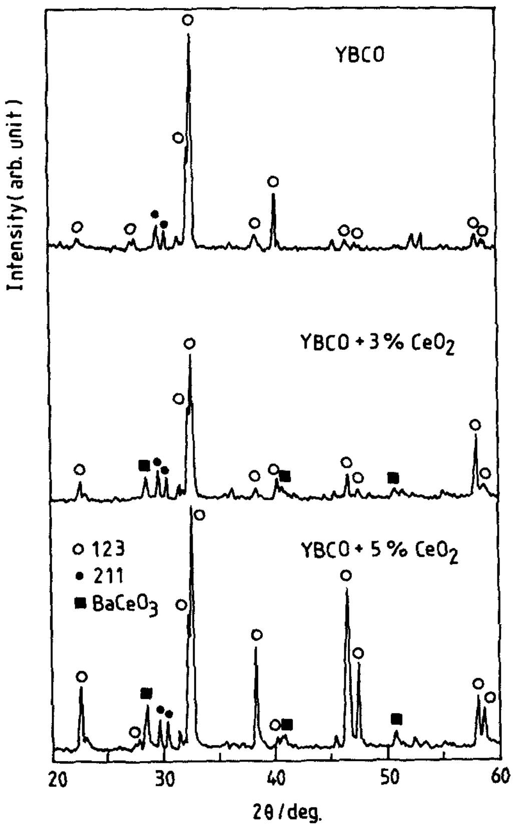

Fig. 4. Powder x-ray diffraction patterns of the CeO_2 added Y-Ba-Cu-O oxides prepared by partial -melt process.

of the unadded sample(a), large textured 1-2-3 grains was observed with 2-1-1 particles trapped in the 1-2-3 matrix. The observed microstructure is known to be a typical feature of Y-Ba-Cu-O oxide prepared by the methods involving the peritectic reaction such as melt-powder-melt-growth[8] and liquid phase process.[9] The trapping of the 2-1-1 particles in the 1-2-3 matrix appears to resulted from the difference between the growth and reaction rate of 1-2-3 phase from 2-1-1 + liquid phase. In the CeO_2-added samples[(b) and (c)], another trapped particles in a 1-2-3 matrix are observed together with 2-1-1 particles. The particles size of this phase is much smaller than that of the 2-1-1 particles. The texture region of the

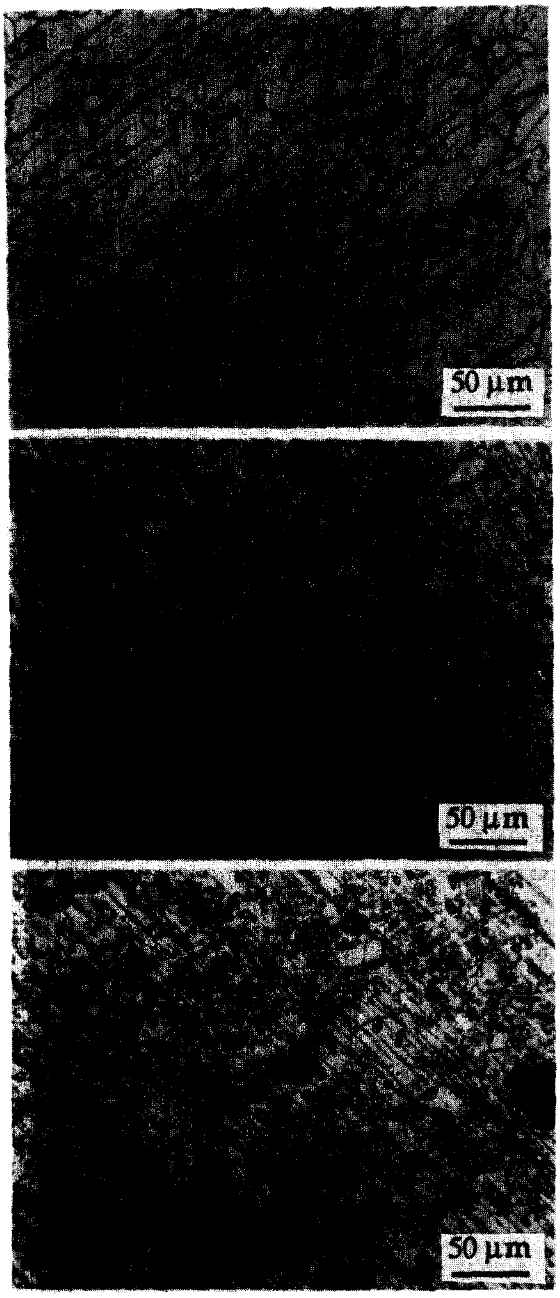

Fig. 5. Optical micrographs of (a) $Y_1Ba_2Cu_3O_y$, (b) 3 wt. % CeO_2-and (c) 5 wt. % CeO_2-added $Y_1Ba_2Cu_3O_y$ showing fine dispersed particles in the 1-2-3 matrix.

1-2-3 grains was reduced with increasing CeO_2 content from 5 mm in the undoped sample to 2mm in the 5 wt. % CeO_2 sample. In order to determime the chemical composition of the fine particle, the SEM EDX analysis was carried out for the 5wt. % CeO_2 sample. Fig. 6 shows the SEM surface micrograph of the sample etched in 1% HNO_3, solution. It was clearly observed that large particles and fine particles were trapped in 1-2-3 matrix with a lot of microcracks. It could be confirmed that the large particles and the smaller ones are 2-1-1 phase and $BaCeO_3$, respectively. This result is consistent with the XRD analysis of Fig. 4. By applying the partial melt process, the dopant could be successively separated from 1-2-3 phase and dispersed in the matrix. The separation of the dopant clearly explains the constant T_c regardless of CeO_2 content illustrated in Fig. 1. The trapped fine particles may be acted as a flux pinning center. Further study is required to understand the effect of the second particle on the critical current density.

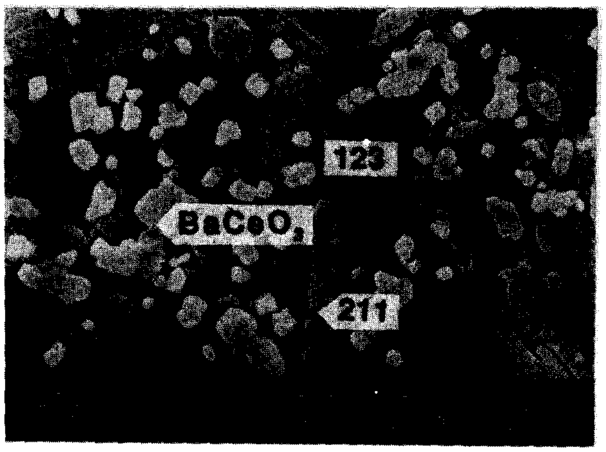

Fig. 6. Scanning electron micrograph of etched surface in 1% HNO_3 solution of the 5 wt. % CeO_2 added $Y_1Ba_2Cu_3O_y$. The large particles and small ones are $Y_2Ba_1Cu_1O_5$ and $BaCeO_3$ phase, respectively.

4. Conclusion

We investigated the effect of CeO_2 addition on the microstructure and superconductivity in the partially by melted Y-Ba-Cu-O superconductors. All the added CeO_2 could be successively separated from 1-2-3 phase by applying the partial melt process. The separation of the dopant from the superconducting phase resulted in the constant T_c regardless of CeO_2 content. The CeO_2 was converted to fine $BaCeO_3$ particles which were trapped in 1-2-3 matrix during the peritectic reaction.

Acknowledgment

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References

1. M. B. Maple, Y. Dalichaouch, J. M. Ferreira, R. R. Hake, B. W. Lee, J. J. Neumeier, M. S. Torikachvili, K. N. Yang and H. Zhou, Physica **B148**, 155(1987).
2. K. N. Yang, B. W. Lee, M. B. Maple and S. S. Laderman, Appl. Phys. **A46**, 229(1988)
3. S. Ohshima and T. Waiyama, Jpn. J. Appl. Phys. **26**, L815(1987)
4. E. V. Sampathikumaran, A. Suzuki, K. Kohn, T. Shibuya, A. Tohdake and M. Ishikawa, Jpn. J. Appl. Phys. **27**, L584 (1988).
5. C. J. Kim, K. B. Kim S. C. Kwon, I. S. Chang and D. Y. Won, Mater. Sci. Lett. **11**, 346 (1992).
6. C. P. Bean, Rev. Mod. Phys. **36** 31(1964).
7. N. McN. Alford, T. W. Button, A. D. Caplin, S. M. Cassidy, J. R. Laverty, D. G. McCartney, R. J. Pollard and Z. X. Shen, Supercond. Sci. Technol. **4**, S238(1991).
8. M. Murakami, M. Morita, K. Doi and K. Koyama, Jpn. J. Appl. Phys. **28**, 1189 (1989).
9. K. Salama V. Selvamanickam, L. Gao and K. Sun, Appl. Phys. Lett. **54**. 2352(1989).