C-Axis Oriented Y-Ba-Cu-O Oxide Superconductor

Shuichi SHIBATA, Takeshi KITAGAWA, Hisaaki OKAZAKI and Takao KIMURA

(Opto-Electronics Laboratories NTT, Tokai-mura, Ibaraki 319-11)

C軸配向 Y-Ba-Cu-O 酸化物超伝導体

柴田修一・北川 毅・岡崎久晃・木村隆男

(NTT 光エレクトロニクス研究所, 319-11 茨城県東海村)

C-axis oriented bulk samples in Y-Ba-Cu-O system have been prepared by the uniaxial pressing technique with various pre-sintering temperatures and pressures. The c-axis orientation by pressing was compared with that of highly c-axis oriented films made by the sol-gel method. Suitable starting compositions and sintering temperatures for preparing c-axis oriented samples were similar in both techniques. The origin of the c-axis orientation was attributed to the growth of plate crystals under the partial melting condition in the sintering process.

[Received May 24, 1989; Accepted August 22, 1989]

Key-words : C-axis orientation, Uniaxial pressing, Sol-gel method, Suitable starting composition, Partial melting

1. Introduction

Anisotropy of electrical and magnetic properties in the c - and a -, b -axes has been reported in $\text{YBa}_2\text{Cu}_3\text{O}_x$ single crystals and epitaxially grown thin films.^{1,2)} Highly c -axis oriented samples are desirable for various applications such as electrical devices because of the high critical current density.

Much effort has been devoted to fabricate high quality oriented superconducting ceramics by various fabrication techniques such as sputtering,²⁾ screen printing,³⁾ spray pyrolysis⁴⁾ and sol-gel method.⁵⁾ We have reported that the highly c -axis oriented film with $T_c(\text{zero})=90$ K can be made on ceramic substrates by the sol-gel method.⁵⁾ It is also found that the suitable starting compositions for the c -axis oriented film are located in Cu-rich and Y-poor side in the Y-Ba-Cu-O compounds. The reason why the degree of c -axis orientation depends strongly on the starting compositions was not yet clear at that investigation stage.

It has been known that c -axis oriented bulk samples can be prepared by uniaxial pressing of pre-sintered superconducting samples. Using this technique, c -axis oriented disk-shaped samples have been prepared and anisotropy in critical magnetic fields of these samples have been examined.^{6,7)}

In this work, c -axis oriented bulk samples in the Y-Ba-Cu-O system have been prepared by using the conventional uniaxial pressing technique with various fabrication parameters. The results in this technique are compared with those

obtained by the sol-gel method.⁵⁾ The preferable starting compositions and sintering temperatures for the orientation, and the influences of the orientation on the electrical properties are compared in both techniques. The origin of the c -axis orientation is discussed on the basis of the suitable conditions for fabricating c -axis oriented samples by these techniques.

2. Experimental procedures

Reagents of Y_2O_3 , BaCO_3 and CuO were weighed to a certain molar ratio and mixed for 1 h. The mixture in Pt crucible was pre-sintered at $900^\circ\text{--}1050^\circ\text{C}$ for 1-10 h in an oxygen atmosphere and was cooled slowly to room temperature at a rate of less than $1^\circ\text{C}/\text{min}$. The resultant pre-sintered bulks were milled in a mortar for 0.5 h and were pressed into pellets by uniaxial pressure. Schematic illustration for c -axis orientation by pressing is shown in Fig.1. The

Fig.1. Schematic illustration of uniaxial pressing for c -axis orientation. Plate like crystals are formed in pre-sintering process and are oriented by pressing.

compositions of the samples in Y-Ba-Cu-O system are shown in Fig. 6, which is the same region as in the sol-gel method (see Fig. 3 of Reference 5)). Only the pellets which were used in the measurements of electrical properties were re-sintered at 875°C for 1 h in an oxygen atmosphere to increase mechanical strength. Since re-sintering at temperatures higher than 900°C decreased the degree of *c*-axis orientation, the condition of 875°C 1 h was chosen. The electrical resistivity of re-sintered samples was measured by the conventional four-probe technique. X-ray diffraction patterns of the samples were taken at each processing step; after pre-sintering, pressing, and re-sintering. Pellet densities were estimated from the size and weight.

3. Results

The X-ray diffraction patterns for $\text{YBa}_2\text{Cu}_3\text{O}_x$ pressed pellets made by pressing with various pressures are shown in Fig. 2. The samples were pre-sintered at 950°C for 10 h, milled for 0.5 h and then pressed into the pellets. Compared with (110) (103) peaks, intensities of (00 *n*) (*n*=1-7) increase with increasing the pressure. *C*-axis

Fig. 2. X-ray diffraction patterns for $\text{YBa}_2\text{Cu}_3\text{O}_x$ pressed pellets. The samples were pre-sintered at 950°C, milled and then pressed into the pellets.

orientation proceed with increasing the pressure.

In preliminary experiments, it was found that the degree of the *c*-axis orientation depends strongly on milling time of pre-sintered samples as shown in Fig. 3. Degree of *c*-axis orientation for pressed pellet were plotted against the milling time. Here, the degree is represented by the X-ray peak ratio of (006)/((110)(103)), for convenience. Milling longer than 1 h remarkably decreased the orientation. Therefore, all the experiments described hereafter were carried out using the samples milled for 0.5 h.

Change in the peak ratio of (006)/((110)(103)) as a result of pressing with pressures from 1 kg/cm^2 to $28 \times 10^3 \text{ kg/cm}^2$ is shown in Fig. 4. Pre-sintering of the samples was carried out at 950°C for 10 h.

The degree of the orientation increases with increasing the pressure, and then decreases slightly at pressures larger than $20 \times 10^3 \text{ kg/cm}^2$. The degree also depends on the compositions of starting Y-Ba-Cu-O compounds. The samples of Cu-rich composition (Y=5, Ba=25, Cu=70 mole%) showed higher degree than that of the 1-2-3 composition (Y=16.7, Ba=33.3, Cu=50 mol%).

Change in pellet densities by pressing is shown in Fig. 5. Here the Cu-rich composition is Y=5, Ba=25 and Cu=70 mol%. The density increases with increasing pressure and reaches constant values.

Compositions of starting Y-Ba-Cu-O compounds are plotted in a ternary system graph in Fig. 6. Samples were pre-sintered at 950°C for 10 h and pressed with pressure of $6.3 \times 10^3 \text{ kg/cm}^2$. Figures near circles show X-ray peak ratios of (006)/((110)(103)). Higher orientation than

Fig. 3. Degree of the *c*-axis orientation vs milling time of pre-sintered sample. An arrow at 0.5 h shows the milling time used in the experiments.

Fig. 4. Change in the peak ratio ((006)/(110))(103) as a function of pressure in the pressing process. Here, open circles and closed circles show the data for 1-2-3 composition (Y=16.7, Ba=33.3, Cu=50 mol%) and Cu-rich composition (Y=5, Ba=25, Cu=70 mol%), respectively.

Fig. 5. Change in density by pressing. Cu-rich composition is Y=5, Ba=25 and Cu=70 mol%.

that of the sample of 1-2-3 composition is achieved at the compositions of Cu-rich and Y-poor side. The suitable composition region for the *c*-axis orientation agrees well with that for obtaining a highly *c*-axis oriented film by the sol-gel method.⁵⁾

Influence of pre-sintering temperature on the

Fig. 6. Composition of starting Y-Ba-Cu-O compounds. Figures show X-ray peak ratios of (006)/(110) (103). A closed circle is for the 1-2-3 composition.

Fig. 7. Degree of the *c*-axis orientation against pre-sintering temperature.

orientation of the pressed pellets is shown in Fig. 7. For comparison, the results for sol-gel oriented films of Cu-rich composition (Y=3.9, Ba=35, Cu=61.1 mol%) are also plotted in the figure. Degree of the orientation of 1-2-3 composition made by pressing increases with increasing the pre-sintering temperature and shows a maximum at 1000°-1050°C. On the other hand, the samples of Cu-rich composition (Y=5, Ba=25, Cu=70 mol%) shows sharp maximum at 950°C. The degree for the sol-gel film is about three times as large as that of the conventional

Fig. 8. Resistivity vs temperature curves for *c*-axis oriented $\text{YBa}_2\text{Cu}_3\text{O}_x$ pellets after re-sintering at 875°C .

Fig. 9. Effect of the *c*-axis orientation on $T_c(\text{zero})$ and resistivity of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ pellets.

pressing. Resistivity vs temperature curves for *c*-axis oriented $\text{YBa}_2\text{Cu}_3\text{O}_x$ pellets (re-sintered at 875° for 1 h) shown in Fig. 8. Resistivity decreases and $T_c(\text{zero})$ shifts to 90 K with increasing the pressure in pressing process. It is noted that the results for $22 \times 10^3 \text{ kg/cm}^2$ and $13 \times 10^3 \text{ kg/cm}^2$ pressed samples are reversed, which corresponds to the decrease of the orientation at high pressure (see Fig. 4).

The effect of the *c*-axis orientation on $T_c(\text{zero})$ and resistivity caused by uniaxial pressing are summarized in Fig. 9. $T_c(\text{zero})$ shifts to 90 K and resistance decreases with increases the degree of the *c*-axis orientation.

4. Discussion

Although $\text{YBa}_2\text{Cu}_3\text{O}_x$ superconducting oxide

crystal (orthorhombic phase) has a unit cell of $a = 3.88 \text{ \AA}$, $b = 3.82 \text{ \AA}$ and $c = 11.68 \text{ \AA}$,⁷⁾ plate like crystal is formed from the unit cells as shown in Fig. 1. A plate crystal can be seen in the growth of single crystal.⁸⁾ Therefore, it is reasonable to consider that oriented sample with *c*-axis perpendicular to the pellet plane can be obtained by uniaxial pressing. The degree of the orientation depends on how the plate crystals are formed successfully in sintering process.

Suitable starting compositions for *c*-axis orientation by the pressing technique (Cu-rich and Y-poor compositions) agree well with those for the sol-gel technique. Melting point of CuO (1148°C) is the lowest among the starting reagents and the Cu-rich and Y-poor composition region is known to be a partial melting region.⁹⁾ The suitable pre-sintering temperatures for the *c*-axis orientation can be also attributed to the partial melting. The appropriate temperatures, $1000^\circ\text{--}1050^\circ\text{C}$ for the 1-2-3 composition, and 950°C for the Cu-rich composition, agree well with the partial melting temperatures for those compositions.¹⁰⁾ Consequently, the *c*-axis orientation by the uniaxial pressing and that in the sol-gel film are attributed to the same origin; growth of plate crystals under the partial melting condition.

However, some differences exist between the results of the pressing technique and the sol-gel technique. The degree of the orientation for the sol-gel film was drastically higher than that obtained by the pressing technique in which commercially available reagents were used. Moreover, the composition change in sintering process is remarkable in the sol-gel method,⁵⁾ while the change in pre- and re-sintering processes was very small in the pressing technique. In the sol-gel method, although the starting compositions of the films are Cu-rich side, their resultant compositions approach the 1-2-3 ratio after sintering, as shown in Reference 5). The difference of the sample properties is considered to be due to the particle size difference in commercially available powder (micron order) and sol-gel powder (less than submicron).

Relatively higher $T_c(\text{zero})$ in the highly *c*-axis oriented film made by sol-gel method is the result of the high *c*-axis orientation. As shown in Figs. 8 and 9, highly oriented samples showed a high $T_c(\text{zero})$.

It should be noted that the plate crystals were easily crushed by milling, as shown in Fig. 3. The decrease in the degree of orientation at high pressure also seemed to be the collapse of the plate crystals by high pressure. It is known that

the true uniaxial pressure is saturated when the applied pressure exceeds a certain limit because of the repulsion from the surface of the apparatus. The saturation of the densities reflects this influence. However, the decrease of the orientation at a high pressure cannot be explained by the phenomena.

The similar results about the *c*-axis orientation were pointed out by the authors in other superconducting oxide systems such as Bi-Sr-Ca-Cu-O (low T_c phase) and Bi-Sr-Ca-Cu-Pb-O system (high T_c phase).¹¹⁾

5. Conclusion

C-axis oriented bulk samples in Y-Ba-Cu-O system were prepared by uniaxial pressing technique with various pre-sintering temperatures and pressures. The results of the *c*-axis orientation in the bulk samples by pressing were compared with those for the films made by the sol-gel method. The following conclusions were obtained.

(1) Suitable starting compositions and sintering temperatures for the *c*-axis orientation are similar in both techniques.

(2) The *c*-axis orientation results in the high T_c (zero) and low resistivity.

(3) Formation of plate crystals in sintering process under the partial melting condition seems to be the origin of the *c*-axis orientation in both methods.

Acknowledgments The authors would like to thank to T. Eda Hiro and N. Uchida for their useful suggestions. They also would like to thank to Ms. M. Miyamoto for her help with the measurements.

References

- 1) Y. Hidaka, Y. Enomoto, M. Suzuki, M. Oda, A. Katsui and T. Murakami, *Jpn. J. Appl. Phys.*, **26**, L726-28 (1987).
- 2) Y. Enomoto, T. Murakami, M. Suzuki and K. Moriwa-ki, *Jpn. J. Appl. Phys.*, **26**, L1248-50 (1987).
- 3) M. Kawasaki, S. Nagata, Y. Sato, M. Funabashi, T. Hasegawa, K. Kishio, K. Kitazawa, K. Fueki and H. Koinuma, *Jpn. J. Appl. Phys.*, **26**, L740-42 (1987).
- 4) H. Niu, N. Fukushima and H. Yoshino, Symposium on the Chemistry of Superconducting Materials, Kyushu University, Oct 15, 1987.
- 5) S. Shibata, T. Kitagawa, H. Okazaki and T. Kimura, *Jpn. J. Appl. Phys.*, **27**, L646-48 (1988).
- 6) L. Lynds, F. Galasso, F. Otter, B.R. Weinberger, J.I. Budnick, D.P. Yang and M. Filipkowski, *J. Am. Ceram. Soc.*, **71**, C130-32 (1988).
- 7) K. Takita, H. Akinaga, H. Katoh, T. Uchino, T. Ishigaki and H. Asano, *Jpn. J. Appl. Phys.*, **26**, L1323-25 (1987).
- 8) D.L. Kaiser, F. Holtzberg, B.A. Scott and T.R. McGuire, *Appl. Phys. Lett.*, **51**, 1040-42 (1987).
- 9) R.S. Roth, J.R. Dennis and K.C. Davis, *Adv. Ceram. Mat.*, **2**, 303-12 (1987).
- 10) T. Sugai, G. Oya and S. Imai, 4 a-KanB-4, The 49 th Autumn Meeting of The Jpn. Soc. Appl. Phys., (1988).
- 11) S. Shibata, T. Kitagawa, H. Okazaki and T. Kimura, F5.127, Mat. Res. Soc. Fall Meeting, Boston, MA, 1988.