Fabrication of large Eu-Ba-Cu-O bulk superconductors for compact NMR magnet

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Abstract. We have investigated the fabrication and position dependence of superconducting properties of large melt-textured Eu-Ba-Cu-O bulk superconductors for the purpose of application as a compact NMR magnet. We successfully fabricated $c$-axis oriented single-grain bulk samples up to 65 mm in diameter by melt-processing under a low oxygen partial pressure. The samples of 32 and 47 mm diameters could trap magnetic fields of 1.4 and 1.7 T at 77 K, respectively. $T_c$ in the sample of 33 mm diameter is almost similar throughout the sample. In 65 mm-sized sample, however, $T_c$ and $J_c$ lowered in inner region of the sample, leading to lowering of maximum trapped field.

1. Introduction
Melt-textured RE-Ba-Cu-O (RE: rare earth elements) bulk superconductors can trap large magnetic fields and thus can function as a strong quasi-permanent magnet [1, 2]. The $c$-axis oriented RE-Ba-Cu-O bulk samples with strong pinning have significant potential for high-field engineering applications. The new type NMR system is one of the most promising applications of bulk superconducting magnet [3]. Large and thick RE-Ba-Cu-O bulk superconductor with a hole can produce homogeneous magnetic field in the center of a hole. It is expected that a small and easy-to-use NMR spectrometer can be assembled using the bulk superconducting magnet. Up to now, $^1$H NMR signal less than 800 Hz signal width at 4.7 T (200 MHz) by 0.3 mm diameter micro coil has been observed using Gd-Ba-Cu-O bulk superconductors [4].

For the improvement of homogeneity of magnetic field in NMR magnet, it is necessary to enlarge the diameter and thickness of bulk superconducting magnet and improve the uniformity of $J_c$ distribution in the bulk material. The select of RE element is also important to achieve further homogeneous magnetic field [5], since paramagnetic moment of RE ion reduces the homogeneity of trapped field by overlapping induced moment during applying external field. Gd- and Dy-Ba-Cu-O bulk materials do not appear to be suitable to achieve extreme homogeneous magnetic field due to the large paramagnetic moment of Gd and Dy ions. Therefore, we now attempt to fabricate large single-grain bulk superconductors containing rare earth ions with small paramagnetic moment such as Eu,
Sm and Y. The Eu-Ba-Cu-O bulk superconductor is expected to have excellent field trapping abilities as well as other light rare earth systems such as Nd-, Sm- and Gd-Ba-Cu-O bulk superconductors. On the preparation and properties of Eu-Ba-Cu-O large bulk superconductor, however, very few studies have been reported. S. Haseyama et al. [6] succeeded in fabricating the single-grain Eu-Ba-Cu-O bulk sample of 45 mm diameter in air. The trapped magnetic field was a low value of 0.4 T at 77 K, due to some small defects such as cracks or high angle grain boundaries. In this paper, we report the fabrication and superconducting and field trapping properties of large c-axis oriented Eu-Ba-Cu-O bulk superconductors up to 65 mm diameter under a low oxygen partial pressure, for the purpose of development of a compact NMR magnet.

2. Experimental

The Eu-Ba-Cu-O bulk samples were synthesized from commercial EuBa2Cu3Oy (Eu123) and sintered EuBa2Cu4Oy (Eu211) powders as starting materials. The Eu211 starting powder was prepared from Eu2O3, BaO2 and CuO powders, which were well mixed and calcined at 950°C for 4 h. The powders of Eu123 and Eu211 were mixed in a molar ratio of Eu123:Eu211 = 5:2. 0.5 wt.% Pt and 20 wt.% Ag2O were also added to the mixtures. The mixed powder was first uni-axially pressed into pellets of 40, 60 and 80 mm diameters, and subjected to cold-isostatic pressing (CIP) under a pressure of 200 MPa. Melt-processing was performed under a controlled oxygen partial pressure of 1%O2 in Ar. The precursors were partially melted at 1100°C for 0.5 h (1 h in the case of 80 mm-sized precursor). Then they were cooled to 1015°C in 1 h, and a melt-textured Nd123 (001) bulk seed crystal about 2 mm in diameter was placed on the top of the melted pellet. After seeding, the precursor was cooled to 990°C in 1 h and slowly cooled at a rate of 0.1-0.5°C/h to 955°C and finally cooled at a rate of 10-50°C/h to room temperature. During melt-processing, the temperature gradient of about 2°C/cm was applied in a furnace where the upper part was in lower temperature. The melt-textured sample was annealed at 400-450°C for 200-500 h in flowing oxygen gas. As a comparison, we also synthesized the Ag added Sm-Ba-Cu-O bulk sample using the 40 mm-sized precursor with the composition of Sm123:Sm211=5:2 with 0.5 wt.%Pt and 20 wt.%Ag2O.

Several specimens with dimensions of about 2 mm×2 mm×1 mm were cut from the oxygen-annealed bulk samples. Measurements of $T_c$ were performed with a Quantum Design SQUID magnetometer in an applied magnetic field of 10 Oe. For the determination of $J_c$, magnetization loops were measured at 77 K up to 5 T for fields parallel to the c-axis. The distribution of trapped field was measured with an automated Hall probe measurement system. The bulk samples were cooled to liquid nitrogen temperature in the presence of 5 T applied parallel to the c-axis. After the removal of the external field, the profile of trapped magnetic flux density was measured by scanning a Hall probe sensor.

3. Results and discussion

When the initial diameters of precursors were 40, 60 and 80 mm, the final dimensions of melt grown bulk samples were reduced to 33, 47 and 65 mm, respectively. Figure 1 shows photographs of as-grown bulk samples 65 mm in diameter and 25 mm in thickness. One can see that the grain was grown from the Nd123 seed crystal and extended to the edge, which indicates that a single domain.
sample could successfully be fabricated.

It is known that superconducting properties of large grain bulk samples often vary with relative positions within a bulk. In the application of bulk superconductors as a NMR magnet, the spatial $J_c$ distribution in the bulk material affects the homogeneity in magnetic field of NMR magnet. Hence we measured $T_c$ and $J_c$-$B$ properties at various locations in the bulk samples. Figure 2(a) shows the temperature dependence of dc susceptibility for small specimens cut from the Eu-Ba-Cu-O bulk sample of 33 mm diameter, and figure 2(b) shows the $J_c$-$B$ curves at 77 K for the specimens. The location of the specimens is displayed in the inset of figure 2(a). As a comparison, the superconducting properties of Sm-Ba-Cu-O bulk sample with the similar size of 33 mm diameter are also displayed in figure 3. In the case of Sm-Ba-Cu-O bulk sample, $T_c$ in the central region and near

Figure 2. (a) Temperature dependence of dc-susceptibility and (b) $J_c$-$B$ curves at 77 K for the specimens cut from various positions in the Eu-Ba-Cu-O bulk sample of 33 mm diameter. The position of each specimen was displayed in figure (a). The values of magnetic susceptibility were normalized by the value at 10 K.

Figure 3. (a) Temperature dependence of dc-susceptibility and (b) $J_c$-$B$ curves at 77 K for the specimens cut from various positions in the Sm-Ba-Cu-O bulk sample of 33 mm diameter. The position of each specimen was displayed in figure (a).
seed crystal was lower than the other regions. The \( J_c \) and irreversibility field largely depended on the position of the sample as shown in figure 3(b). The similar results on the Sm-Ba-Cu-O bulk superconductor were reported by H. Ikuta et al. [7]. On the other hand, the Eu-Ba-Cu-O bulk sample 33 mm in diameter revealed a weaker position dependence of superconducting properties. The onset-\( T_c \) values of all the specimens in the Eu-Ba-Cu-O bulk sample were about 94 K with a sharp transition as shown in figure 2(a). In the inner region of the sample, the differences among the \( J_c \)-\( B \) properties of specimens are small compared to the Sm-Ba-Cu-O sample as shown in figure 2(b). It was reported that the position dependences of \( T_c \) and \( J_c \) in the large Sm-Ba-Cu-O and Nd-Ba-Cu-O bulk materials are related to the degree of RE/Ba substitution in the local \( RE_{1+x}Ba_{2-x}Cu_3O_y \) solid state phase. The weak position dependences of \( T_c \) and \( J_c \) in the Eu-Ba-Cu-O sample are probably due to a smaller range of RE/Ba substitution in Eu-Ba-Cu-O than Sm-Ba-Cu-O, since Eu\(^{3+}\) ion is smaller than Sm\(^{3+}\) ion. The high \( T_c \) and sharp superconducting transition exhibit the suppression of Eu/Ba substitution throughout the bulk sample.

The position dependence of \( T_c \) and \( J_c \) of the larger Eu-Ba-Cu-O sample of 65 mm diameter was also studied. As revealed in figure 4(a), the temperature dependence of dc magnetization for each specimen in upper surface area is almost similar. However, as revealed in figure 4(b), the onset-\( T_c \) of the specimens in inner region varied from 88 K to 94 K depending on the position of bulk sample, that is, \( T_c \) decreased with the distance from edge of the sample. The low \( T_c \) value in inner region of this large sample will be caused by the residual oxygen after partial melting, as proposed on the large Sm-Ba-Cu-O bulk superconductor [8]. RE123 phase in the RE-Ba-Cu-O samples releases \( O_2 \) gas when the sample is partially melted. In RE-Ba-Cu-O materials including light rare earth element, RE/Ba substitution is promoted with increasing oxygen content, leading to lowering of \( T_c \). If the \( O_2 \) gas remains in the sample during crystal growth, it increases the RE/Ba substitution. In the case of the large Eu-Ba-Cu-O sample of 65 mm diameter, it will be difficult to remove \( O_2 \) gas from the melted sample compared to the sample of 33 mm diameter. Figure 5 shows the \( J_c \)-\( B \) curves for the specimens cut from the 65 mm-sized sample. As shown in figure 5(b), the \( J_c \) in the specimens cut from the inner region of the sample lowered, corresponding to low \( T_c \) values in these positions.

Figure 6 shows the trapped magnetic field distributions of the Eu-Ba-Cu-O samples of 33, 47 and 65 mm diameters and the Sm-Ba-Cu-O sample of 33 mm diameter. The profiles exhibited a symmetric distribution, indicating that each sample consists of single-grain. The Eu-Ba-Cu-O bulk sample 33 mm in diameter shows the maximum trapped field of 1.4 T, which is comparable to that of

![Figure 4](image-url)
Sm-Ba-Cu-O with the similar size (1.3 T). Furthermore, the Eu-Ba-Cu-O sample of 47 mm diameter could trap 1.7 T. This value is about four times higher than that of the Eu-Ba-Cu-O bulk sample of 45 mm diameter reported by S. Haseyama et al. [6] Such high values of trapped fields imply that the Eu-Ba-Cu-O have significant potential as a strong bulk superconducting magnet. However, as shown in figure 6(d), the trapped field of the sample of 65 mm diameter was 1.3 T. Such a low value results from the poor superconducting properties in the central region of this sample.

For the actual application of RE-Ba-Cu-O bulk superconductor as a NMR magnet, it is required to increase the size of sample and improve homogeneity of magnetic field. In this work, we succeeded in fabricating the large Eu-Ba-Cu-O bulk sample up to 65 mm in diameter. Nevertheless, the homogeneity in superconducting properties of the large sample is still unsatisfactory at the present stage. Further investigation is required to improve $T_c$ in inner region of the sample. We believe that the sufficient homogeneity of magnetic field is achieved by some methods to depress RE/Ba substitution such as the remove of residual oxygen with extension of holding time at partial melting stage [8], the selection of Ba-rich composition [9] and the annealing of as-grown sample in Ar gas [10].

4. Conclusions
We have been studied the fabrication and superconducting properties of large melt-textured Eu-Ba-Cu-O bulk superconductors for the purpose of development of a compact NMR magnet. We successfully fabricated $c$-axis oriented single-grain bulk samples up to 65 mm in diameter by melt-processing under a low oxygen partial pressure. The samples of 32 and 47 mm diameters could trap magnetic fields of 1.4 and 1.7 T at 77 K, respectively. $T_c$ and $J_c$ in the sample of 33 mm diameter are almost uniform compared to Sm-Ba-Cu-O sample with similar size. In 65 mm-sized sample, however, $T_c$ and $J_c$ lowered in inner region of the sample, leading to lowering of maximum trapped field. For the application as a NMR magnet, further improvement in the homogeneity of superconducting properties of the large sample is required. This will be achieved by the depression of Eu/Ba substitution in near future.

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Figure 6. Trapped magnetic field distribution of the bulk samples of Eu-Ba-Cu-O and Sm-Ba-Cu-O with various sizes at 77 K (1 dev. =0.1 T). The total gap between the polished top surfaces of the sample and the active area of the Hall sensor was adjusted to be 1.2 mm.

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