Homogenizing field-trapping capabilities of bulk Y-Ba-Cu-O superconductors using Ba-Cu-O oxide substrate for practical applications

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Abstract. We employed Ba-Cu-O substrates for fabrication of bulk Y-Ba-Cu-O superconductors in the top-seeded melt-growth method. There were several advantages for a use of a Ba-Cu-O substrate compared to conventional substrate materials such as MgO, ZrO₂, Al₂O₃, RE123 and RE211 (RE = rare earth). The Ba-Cu-O substrate avoided crystallization from a substrate, suppressed a liquid loss and then scarcely reacted with a precursor. Furthermore, the introduction of large-sized cracks into a grown bulk greatly was suppressed by propagating along the interface between a grown bulk and a substrate. We could obtain bulk Y-Ba-Cu-O superconductors with uniform trapped magnetic filed distributions and equal maximum trapped filed values on both top and bottom surfaces, which indicates that the field-trapping capabilities were homogenized along the c-axes of the bulks fabricated on the Ba-Cu-O substrates.

1. Introduction
A top-seeded melt-growth (TSMG) technique has made it possible to produce large c-axis oriented bulk superconductors several cm in diameter, accompanied by an enhancement of critical current densities (Jc) in virtue of the refinement of secondary phase particles dispersed in a matrix [1 - 4]. The peritectic reaction: REBa₂Cu₃O (RE123) \( \rightarrow \) RE₂BaCuO (RE211) + L (RE = rare earth, L: liquid phase \((3BaCuO₂ + 2CuO))\) is essential for bulk fabrication techniques including the TSMG in order to obtain a large single grain. A precursor pellet therefore is once heated above the peritectic temperature and cooled to grow a grain. Unfortunately, a long time is generally required to obtain a large single grain due to a low growth rate. Although such TSMG-processed bulk superconductors could exceed 3T in trapped magnetic field of a top surface at liquid nitrogen temperature [5], large-sized cracks affecting a trapped magnetic field distribution are readily formed by such as porosity, segregation, micro-cracks, thermal stress and oxygen annealing for a transformation to a superconducting phase in enlarging the

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size of bulks. Particularly, a long-time thermal treatment around the peritectic temperature caused a reaction and/or a fixation between bulk bottom surfaces and substrate materials, which was a key trigger of cracking due to a concentration of thermal stress and a brittleness of reacted regions [6]. Furthermore, such a reaction of precursors with substrate materials at the bottoms increased a liquid loss and then degraded field-trapping capabilities and superconducting properties [6]. So far, our interest was to improve the homogeneity of field-trapping capabilities along the thickness direction (c-axis) of bulks for practical applications. Hence, we have investigated the effect of substrate materials particularly on the field-trapping capabilities at the bottom surfaces of bulks. We have clarified that Ba-Cu-O compounds are suitable as substrates to drastically suppress a reaction with bulks, a liquid loss and crack propagation as shown in the figure 1, which can greatly improve the field-trapping capabilities along the c-axes of bulk Nd-Ba-Cu-O superconductors [6]. A bulk Y-Ba-Cu-O superconductor with a stoichiometric Y123 superconducting phase is more applicable to practical engineering than a bulk Nd-Ba-Cu-O since a larger bulk is readily obtainable.

In this work, we employed Ba-Cu-O substrates in the production of TSMG-processed bulk Y-Ba-Cu-O superconductors and investigated their effects on the crystal growth, field-trapping capabilities, microstructures and superconducting properties.

2. Experimental

The precursor powders with initial composition of Y123: Y422 = 5: 1 + 0.5mass%Pt were thoroughly mixed for 2h and then uniaxially pressed into pellets of 30mm in diameter and 13mm in thickness at a pressure of 2kPa. The precursor pellets were subjected to a TSMG process in air, where one precursor was placed on a substrate of compacted BaCuO2 powder and meanwhile the other was placed on a conventional YSZ substrate for comparison, as schematically presented in the figure 2. The compacted BaCuO2 powder was placed on a layer of compacted Yb2O3 powder on an YSZ plate in order to stably keep the molten BaCuO2 under the partially molten precursors. Although a part of BaCuO2 powder reacted with an Yb2O3 powder during the processing, an excess amount of BaCuO2 was added to avoid the reaction. The thermal profiles for the TSMG process in this study are described as follows. The precursors were heated to 1373K in 5h, held for 1h and then cooled down to 1303K in 0.5h to put a c-axis aligned Nd123 seed crystal. The partially molten precursor with an Nd123 seed was cooled down to 1263K in 0.5h and gradually cooled at a rate of 0.5K/h to 1243K in order to grow a c-axis aligned single grain. Finally, a grown bulk was subjected to the furnace cooling to air temperature in 20h. Final dimensions of the grown bulks were 26mm in diameter and 10mm in thickness after the substrates and seeds were removed, and then both top and bottom surfaces were parallelized by polishing. The grown bulks were oxygenated at 673K for 100h. Visual investigation was performed after polishing both top and bottom surfaces of the grown bulks. The trapped magnetic field distributions of the bulk fabricated on the BaCuO2 substrate were measured at both top and bottom surfaces in liquid nitrogen by a Hall sensor two-dimensionally scanning at 1mm above the surfaces. SEM observation was performed on the cross sections at the bulk bottoms, which were produced on the different substrates before removing the substrates in order to evaluate crystal growth behaviour and crack propagation from the substrates. Furthermore, small specimens were cut from the
grown bulks in order to investigate the effect of the BaCuO$_2$ substrate on microstructures and normalized dc-susceptibilities by a microscope and a quantum design SQUID magnetometer, respectively.

![Figure 2. Schematic illustrations of the sample setups: (a) BaCuO$_2$ and (b) YSZ substrates.]

3. Results and discussion

3.1. Effect of BaCuO$_2$ substrate on suppression of crack propagation into grown bulk

Figure 3 shows the bottom surfaces of bulk Y-Ba-Cu-O superconductors fabricated on the different substrates. Here, the substrates were removed and then both top and bottom surfaces of the bulks were polished. In both cases, $c$-axis aligned single grains apparently grew from the Nd123 seeds to the peripheries of bulks on the top surfaces. As presented in the figure 3, the bottom surface of the bulk on a BaCuO$_2$ substrate scarcely contained large-sized cracks and reacted regions while the other on a conventional YSZ substrate contained many large-sized cracks. Such a big difference was also confirmed in the Nd-Ba-Cu-O bulks, which was already shown in the figure 1 [6]. Moreover, since some other grains individually nucleated and grew from the YSZ substrate in parts of the bulk bottom, the $c$-axes of them were randomly oriented. SEM observation was performed to investigate the difference of cracking behaviour on the bottom cross sections along the thickness direction, which was presented in the figure 4. In the case of the YSZ substrate, there were some regions in contact with the substrate, which were not crystallized presumably due to a local compositional change caused by a liquid loss during the TSMG process. Furthermore, many large-sized cracks propagated from the substrate into the grown crystal, which were presumably induced by the thermal stress, the fixation to and reaction with the substrate and so on. On the other hand, in fabricating the bulk on the BaCuO$_2$ substrate, large-sized cracks tended to propagate along the interface between the grown crystal and the substrate. The cracking behaviour was quite different from each other. Ba$^{2+}$ and Cu$^{2+}$ ions of a BaCuO$_2$ substrate are main components of a liquid phase in the partially melting state and hence some amount of Ba$^{2+}$ and Cu$^{2+}$ ions may diffuse into and react with a partially molten precursor. However, since the interface seemed to be relatively clear and the melting temperature of BaCuO$_2$ was lower than the decomposition temperature of Y123, the induced thermal stress between the bulk bottom and the substrate was probably relieved by the crack propagation along the interface and the suppression of fixation.

![Figure 3. Photos of the bottom surfaces of Y-Ba-Cu-O bulks 24mm in diameter and 10mm thick fabricated on (a) BaCuO$_2$ and (b) YSZ substrates, respectively. Note that, in the case of a YSZ substrate, there are many cracks and randomly oriented grains growing from the substrate.]

3.2. Field–trapping capabilities of bulk fabricated on BaCuO$_2$ substrate

A BaCuO$_2$ substrate had a beneficial effect on a suppression of cracking in a bulk bottom. Large-sized cracks present on a bulk surface decreased a field-trapping capability and then distorted a trapped magnetic field distribution [6]. Figure 5 shows the trapped magnetic field distributions on both top and bottom surfaces of the bulk fabricated on a BaCuO$_2$ substrate. The symmetrical magnetic distribution with a single peak was obtained on both surfaces. This indicates that there were no large-sized cracks on the bulk surfaces affecting the trapped magnetic field distributions as expected from the visual and SEM observations. Furthermore, the maximum trapped field values on both surfaces were the same values of 0.28T at liquid nitrogen temperature. Such excellent features of the BaCuO$_2$ substrate were also displayed in the Nd-Ba-Cu-O bulks [6]. Since a Y-Ba-Cu-O superconductor has a stoichiometric Y123 phase, Ba$^{2+}$ and Cu$^{2+}$ ions, which diffused from the BaCuO$_2$ substrate into a bulk during the process, do not contribute to suppress the substitution of Ba$^{2+}$ sites for Y$^{3+}$ ions like Nd-Ba-Cu-O. They will therefore form non-superconducting chemical compounds as foreign ones in a matrix and then may depress a field-trapping capability of a bulk if more amount of Ba$^{2+}$ and Cu$^{2+}$ ions diffuses than that of them decreased by a liquid loss. However, the maximum trapped field value on the bottom surface was comparable to that on the top, which explains that a BaCuO$_2$ substrate can contribute to homogenize the filed-trapping capabilities along the c-axis and hence is scarcely detrimental to a quality of bulk superconducting products. On the other hand, the trapped magnetic filed distributions of the bulk fabricated on a YSZ substrate were quite different on the top and bottom surfaces as shown in the figure 6. Particularly on the bottom, the trapped magnetic filed distribution was largely distorted and divided into some peaks by large-sized cracks shown in the figures 3(b) and 4(b). The maximum trapped filed value on the bottom was also as low as 0.05T at liquid nitrogen temperature in comparison with that of 0.17T on the top.

Figure 5. Trapped magnetic distributions on both (a) top and (b) bottom surfaces of Y-Ba-Cu-O bulk fabricated on a BaCuO$_2$ substrate.
3.3. Microstructures and normalized dc-susceptibilities of bulk fabricated on BaCuO$_2$ substrate

We evaluated the effect of a BaCuO$_2$ substrate on the microstructures and normalized susceptibilities for a bulk fabricated on it. Figures 7 and 8 show the microstructures and the normalized dc-susceptibilities ($T_c$), respectively, which were evaluated for the specimens cut from a bulk grown on a BaCuO$_2$ substrate. The spatial positions of the specimens are presented in the inset in the figure 7(a). As shown in the figure 7, Y211 inclusions as pinning sites were uniformly dispersed at both positions although their mean size slightly increased at the bulk bottom. Since the mean Y211 size at various positions in a bulk generally depends on a period until the crystallization from a partially molten precursor and a pushing/trapping behaviour of Y211 particles at a growth interface [7-9], it will increase in some initial compositions and growth conditions. The on-set $T_c$ value in the bottom position was as large as 91K, which was the same as that in the top as presented in the figure 8. However, the $T_c$ transition curve for the bottom slightly was broadened. Hence, the BaCuO$_2$ substrate as liquid phase components locally had the slight potential to affect the mean Y211 size and $T_c$ transition at the bottom although the trapped magnetic filed distribution was uniform and the maximum trapped field value was comparable to that at the top as an overall performance.

Figure 7. Microstructures of specimens cut from (a) top and (b) bottom positions of the bulk fabricated on a BaCuO$_2$ substrate. The positions of specimens were indicated in the inset. The Y211 inclusions are brightly coloured. The mean Y211 size was 1.23 and 1.41µm, respectively.
Figure 8. Normalized dc-susceptibilities of specimens cut from the bulk fabricated on a BaCuO$_2$ substrate. The positions of specimens were indicated in the inset in the figure 7(a).

4. Summary
We produced bulk Y-Ba-Cu-O superconductors on BaCuO$_2$ substrates by the TSMG process. There were several advantages of a Ba-Cu-O substrate over conventional substrate materials. The cracking behaviour at the bulk bottom on the BaCuO$_2$ substrate was quite different compared with a conventionally processed bulk. Large-sized cracks propagated along the interface between a grown bulk and a substrate, which greatly suppressed their penetration into a grown bulk. Furthermore, the BaCuO$_2$ substrate suppressed a crystal growth from a substrate, a liquid loss and a non-grown region caused by a local compositional change. Hence, we could obtain a good quality bulk Y-Ba-Cu-O superconductor like Nd-Ba-Cu-O, which had the uniform trapped magnetic field distributions on both top and bottom surfaces with the equal maximum trapped field values of 0.28T at liquid nitrogen temperature. Such a fact indicates that the field-trapping capabilities were homogenized along the c-axis of the bulks fabricated on the Ba-Cu-O substrate. This simple fabrication technique using a BaCuO$_2$ substrate as main components of a liquid phase is available to all kinds of 123 bulk superconductors. Therefore, it enables to contribute to develop practical applications of bulk superconductors.

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