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Recent Development of Bulk High-Tc Superconductors

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Abstract

Recent development in the field of RE-Ba-Cu-O (REBCO, RE: Y or rare earth elements) bulk high-*Tc* superconductors (HTS) is reviewed in the present paper. After the fatal weak link problem of sintered REBCO superconductors has been overcome by melt processing, this field has been greatly advanced during last ten years. The critical current density J_c at 77 K has been enhanced by introducing effective flux pinning sites into the $REBa_2Cu_3O_y$ (RE123) superconducting matrix. Large melt-textured REBCO bulk crystals have been fabricated with the TSMG(top-seeded melt growth) technique. Mechanical properties of REBCO bulks have been improved by using the Ag additive or epoxy resin. Real bulk applications such as current lead, fault current limiter, flywheel energy storage system, magnetic field source, magnetic separation system, and etc., surely come true near future.

Keywords : bulk high-T_c superconductors, critical current density, flux pinning sites, top-seeded melt growth, bulk applications

I. Introduction

Low J_c values of all sintered HTS bulks, originated from a week link at the grain boundaries, had once offered a serious challenge for real applications. However, after the fatal weak link problem was overcome by producing REBCO bulks with a highly textured microstructure, their J_c values are now high enough to seek real applications with the liquid nitrogen (LN_2) refrigeration. Therefore, various applications, using REBCO bulks as passive devices in response to a permanent magnet or as active devices in the form of superconducting permanent magnets, are under development.

In this paper, at first I briefly review the progress in bulk REBCO superconductors during past years. Current important issues are followed. Then the TSMG process, a key fabrication technique for producing large melt-textured REBCO bulk crystals, is explained. Finally, I describe the present status of bulk applications.

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II. Progress in Bulk REBCO Superconductors

The grain boundary weak links of sintered REBCO, causing the degradation of J_c ($<10^3$ A/cm^2 at 77 K), had once been the most serious problem for real applications. Regarding the weak link problem, a pioneering accomplishment was made by Jin *et al.*[1] in 1988, who achieved large J_c ($>10^4$ A/cm^2 at 77 K and 0 T) from YBCO bulks fabricated by the melt process. While all other researchers tried to obtain a clean gain boundary to overcome the weak link problem at that time, they applied a directional solidification process, usually employed in the field of metallurgy until then, to the oxide ceramics of the Y-Ba-Cu-O system, and their try was successful for producing high-J_c YBCO bulks. Since fabricated YBCO bulks were composed of a highly textured microstructure with a preferred orientation along the c-axis of Y123 crystals, they coined the name of this fabrication process as the melt-textured growth (MTG) process.

After the above report, the field of bulk HTS has been remarkably advanced. First of all, J_c values and its field dependency at 77 K of YBCO bulks have been further improved through the microstructure control. In 1989, Murakami *et al.*[2] reported much improved J_c ($> 10^4$ A/cm^2 at 77 K and 1 T) values for YBCO bulks fabricated by the quenched melt growth (QMG) process. Chemically, YBCO bulks are solidified by the peritectic reaction of Y_2BaCuO_5(Y211) + liquid(L) → Y123 below 1010℃ in air and thus Y211 second phase particles are trapped in the Y123 matrix during solidification. For the control of the Y211 particle size, they tried to use as-quenched chunks from a high-temperature melt molten in the Pt crucible as the precursor. Finally they found that it was very effective to form a semimelt, composed of Y_2O_3 + L, at the temperature above 1240℃ in air before quenching. With this process, they could reduce the average particle size of Y211 inclusions in the Y123 matrix to the submicron level, which resulted in great improvement of J_c. In 1991, this process was advanced to the melt-powder-melt-growth (MPMG) process by Fujimoto *et al.*[3], who pulverized the melt-quenched chunk of the QMG process to obtain a homogeneous mixture of ingredients within as-quenched chunks and then pressed the powder into pellets before the melt growth of the YBCO bulk, which resulted in further J_c improvement and also larger textured domains.

In 1994, high functional REBCO bulks other than YBCO were developed by Yoo *et al.*[4]. They succeeded in fabricating NdBCO bulks with larger J_c values compared with those of MPMG-processed YBCO bulks, even though the Nd422 second phase inclusions within the Nd123 matrix were not refined. Using a reduced oxygen atmosphere (i.e., low oxygen partial pressure) during the melt growth, known as the oxygen-controlled-melt-growth (OCMG) process, they could obtain much larger J_c in high fields at 77 K, as shown in Fig. 1.

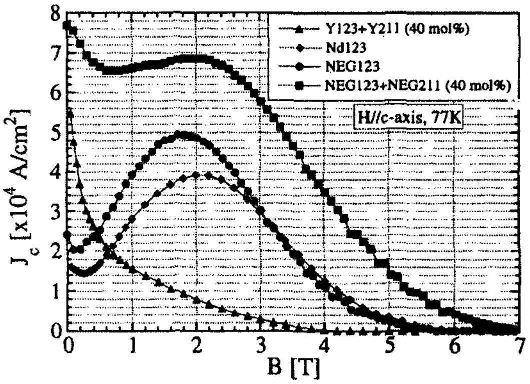


Fig 1. J_c-B curves of MPMG-processed YBCO and various OCMG-processed REBCO bulks at 77 K and for H//c-axis (data from ref. [5]). Where, NEG denotes the mixture of Nd, Eu, and Gd.

The OCMG process was later proved commonly effective for the light rare earth elements(LRE)-Ba-Cu-O systems (LRE: La, Sm, Eu, and Gd)[5,6]. Recently, Muralidher *et al.*[7] have reported that J_c values of OCMG-processed (Nd,Eu,Gd)BCO bulks are also enhanced in low fields by refining the second phase particles (see Fig. 1), which is similar to the case of YBCO bulks.

Field-dependency of J_c is fundamentally related to the effectiveness of the flux pinning sites since supercurrents dissipate if the quantized magnetic flux (sometimes called as vortex or fluxoid) is not properly pinned. In this viewpoint, it can be said that the progress in REBCO bulks has been possible by developing new effective flux pinning sites inside the RE123 superconducting matrix. At present, it is in good agreement that two different types of effective pinning sites exist in bulk REBCO superconductors in the LN2 temperature region (63 ~ 77 K). One type follows an interfacial pinning mechanism and the other type follows a field-induced pinning mechanism.

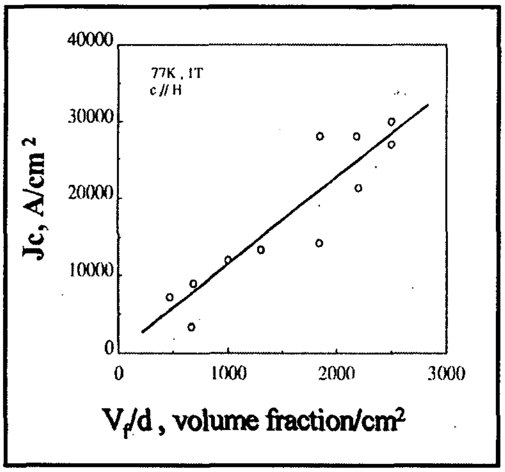


Fig. 2. J_c as a function of V_f/d for YBCO bulks containing various Y211 inclusions (data from ref. [8]). Where, V_f is the volume fraction of Y211 against Y123 and d is the average particle size of Y211.

The RE211(or RE422 for La and Nd)/RE123 interfaces are regarded as the interfacial pinning sites. Thus is well supported by experimental data shown in Fig. 2. Average Y211/Y123 interfacial area, represented by V_f/d, increases with reducing the average particle size of Y211 inclusions in the Y123 matrix. Since J_c values linearly increase with increasing V_f/d, Y211/Y123 interfaces are thus believed to act as effective flux pinning sites.

On the other hand, additional effective pinning centers, responsible for the peak effect in high field region(see Fig.1), exist in LREBCO bulks. Although OCMG-processed LREBCO bulks exhibit high T_c values of 92 - 96 K, LRE-substituted Ba regions of low T_c exist in the LRE123 matrix of high T_c since all LRE123 phases form the $LRE(LRE,Ba)_2Cu_3O_y$-type solid solution. In Fig. 3, the pinning sites are schematically illustrated for NdBCO as a representative of LREBCO. These low-T_c regions are superconducting in low fields and thus may not play a role of effective pinning sites. However, in high fields, these regions will become normal and then turn into effective pinning sites.

It is also known that neutron irradiation is very effective for generating strong flux pinning sites of REBCO bulks[9,10], which demonstrates that further improvement of J_c is possible by developing smaller defects like columnar defects generated by the irradiation damage. Although irradiation methods are surely one way to improve J_c, its application to large REBCO bulks is difficult and moreover, a radiation problem occurs. In this respect, if any, a processing technique to control the second phase inclusions within the RE123 matrix to

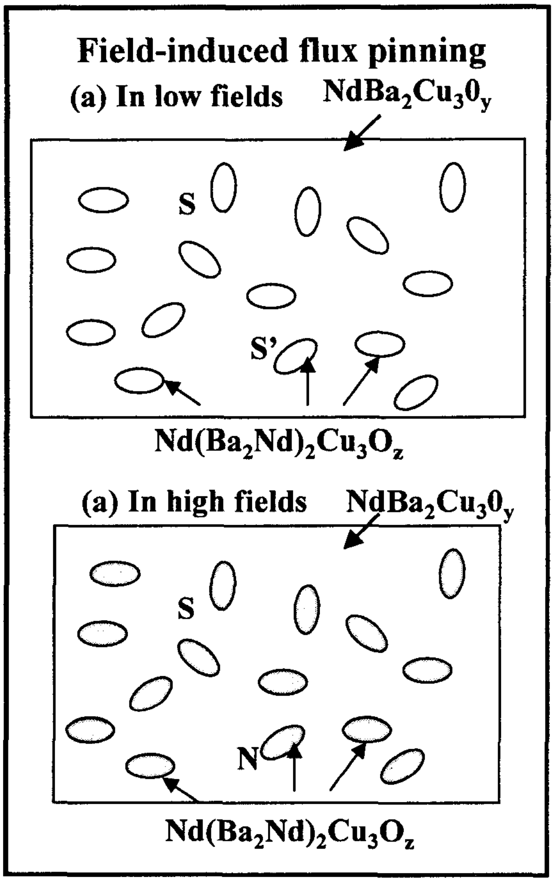


Fig 3. Schematic illustration of the field-induced flux pinning by finely distributed Nd-rich region.

the level of nanometer scale is highly desired for further improvement of J_c.

Fabrication technique of large REBCO bulks has been progressed. Compared with the directional solidification process of MTG, a very simple slow cooling method known as the liquid-phase (LP) process was developed by Salama *et al.*[11]. This process, usually used for a single crystal growth, was later advanced to the TSMG process by Sawano *et al.*[12]. It is now commonly used for the fabrication of large single-domained REBCO bulk crystals. The schematic illustration of the TSMG method is represented in Fig. 4 for producing a single-domained YBCO bulk. In Fig. 4, a seed crystal like Sm123 is located on the top surface of the precursor. With decreasing the temperature slowly, YBCO bulk can be grown from the seed crystal continuously. If the growth condition is carefully controlled, highly textured single-domained YBCO bulks are obtained. This process is also applicable to the fabrication of other REBCO bulks. Fig. 5 represents typical photographs of YBCO bulk crystals grown by the TSSG method. YBCO bulk crystals grow with a rectangular shape although only the top surfaces of samples are imaged in Fig. 5. Faceted growth fronts are (100) and (010) planes.

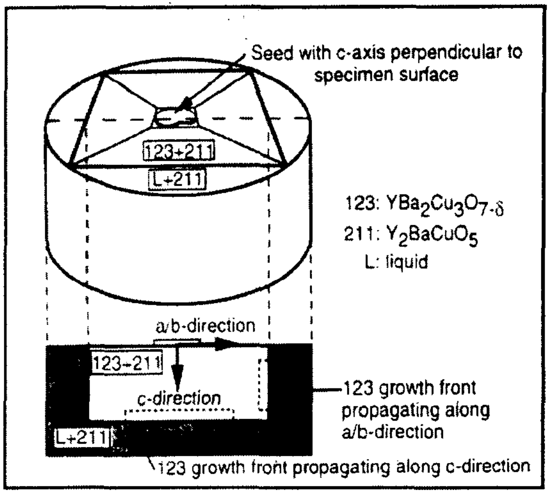


Fig 4. Schematic Illustration of the TSMG Method for the Y-Ba-Cu-O system

Fig. 6 represents the trapped field profile of a YBCO single-domained bulk with 32 mm diameter and 20 mm in thickness fabricated by the TSMG method in our laboratory. If a bulk sample is composed of multiple domains, cracks, or high angle domain boundary, the trapped magnetic flux distribution does not exhibit a single peak anymore but multiple peaks of a degraded flux density. As previously mentioned, OCMG-processed LREBCO bulks possess higher J_c at 77 K in

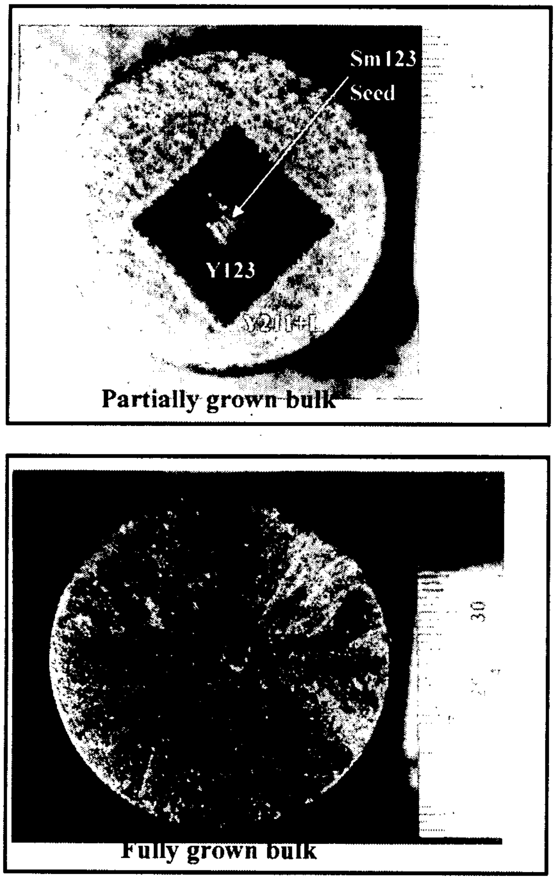


Fig. 5. Typical photographs of YBCO bulk crystals grown by the TSMG Method. Both partially and fully grown samples are represented at the top and bottom, respectively.

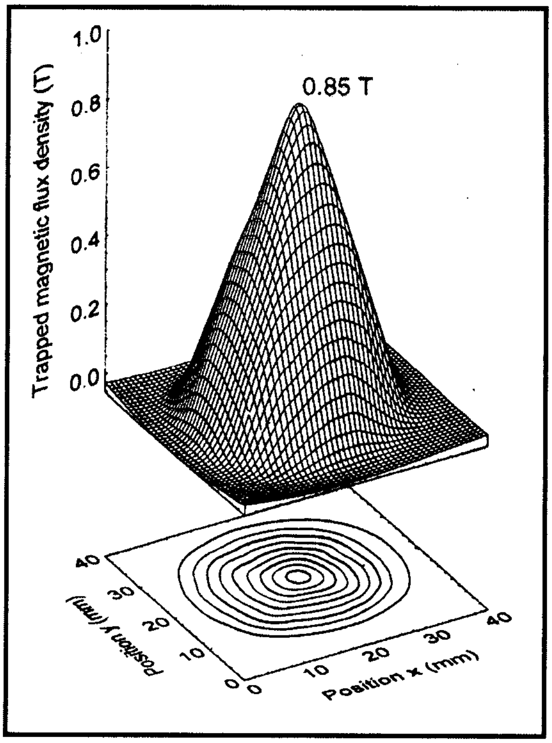


Fig. 6. Trapped field profile of a single-domained YBCO bulk.

comparison with YBCO bulks, which results in higher trapped flux. For a comparison, recent data for an OCMG-processed GdBCO/Ag bulk of 32 mm diameter and 20 mm thickness is represented in Fig. 7. Here, it should be noted that while fabrication of large single-domained YBCO/Ag composite bulks is very difficult, it is much easier to fabricate large single-domained LREBCO/Ag composite bulks although the reason for this phenomenon has not been fully clarified yet. For the identical sample dimension, much higher trapped fields are obtained from GdBCO/Ag composite bulk in comparison with the YBCO bulk in Fig. 6. It is also noteworthy that the field gradient of the GdBCO/Ag bulk in Fig. 7 is different from the YBCO in Fig. 6. The trapped field gradient of GdBCO/Ag at higher fields above ~ 1 T, which corresponds to ~ 2 T within the sample, becomes steeper than that at lower fields while the trapped field gradient of YBCO gradually decreases from the surface to the center of the sample, which represents different J_c-B characteristics at 77 K of these samples.

Currently, there are several important issues in the field of bulk REBCO superconductors. The first issue is further improvement of J_c at 77 K. For this purpose, two approaches are being performed. One is to search for

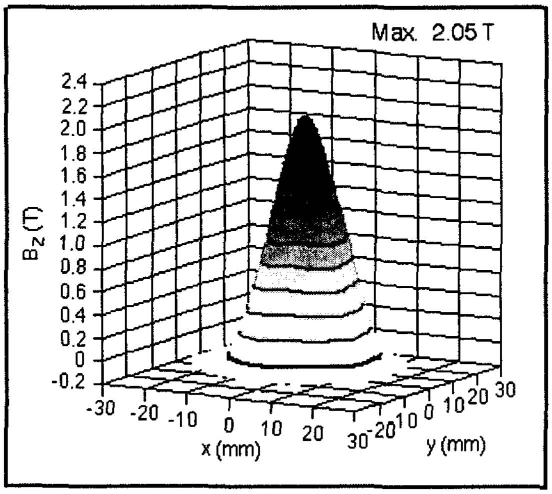


Fig. 7. Trapped field profile of a GdBCO/Ag composite bulk fabricated with the TSMG method in a reduced oxygen atmosphere (1%O_2 + 99%Ar) (data from ref. [13]).

more effective pinning sites through a chemically feasible processing, and the other is to find better materials system among REBCO bulks.

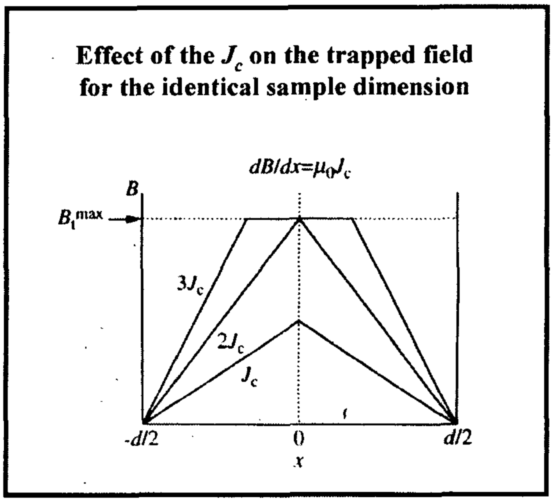
As previously mentioned, irradiated bulks exhibit drastically enhanced J_c over all field region at 77 K, Thus further J_c enhancement will be possible if more effective pinning centers are found. In this respect, discovery of a novel processing, which can produce the second phase inclusions of nanometer size, is highly desired. On the other hand, materials selection has not been optimized yet. As shown in Fig. 1, although it seems better to select the initial batch composition with a mixture of LRE elements for obtaining higher J_c, materials selections have not been fully searched yet. Therefore, a systematic study for an optimum materials selection is greatly required.

The second issue is about the fabrication process of single-domained REBCO bulks without the weak links. Even with an identical thermal profile applied for the TSMG process, single-domained bulks are not highly reproducible at the moment, which becomes more serious with increasing the bulk dimension. While this problem is not so serious for bulk applications as passive devices since the magnetic field generated by a permanent magnet is rather limited below around 0.5 T, it becomes very serious for bulk applications as active devices like superconducting permanent magnets. Therefore, the establishment of reproducible fabrication processing of large single-domained REBCO bulks will become a key technical issue for a mass production.

The third issue is the enhancement of mechanical properties of REBCO bulks. This issue is very critical especially for superconducting permanent magnets since when a high external field applied to activate (or magnetize) superconducting bulks is turned off, bulk samples experience a high loop stress due to the magnetic pressure generated by a very steep field gradient which sometimes causes cracking in REBCO bulks. In order to prevent the crack formation and propagation during the activation, brittleness of REBCO bulks should be handled. For this purpose, several approaches like incorporation of the Ag additive or infiltration of a resin have been performed.

III. Bulk Applications

Applications of bulk REBCO superconductors may be classified into three major categories: current-carrying conductors, passive devices, and active devices. Since J_c of REBCO bulks is very high at 77 K, large currents above 1,000 amperes can be easily transported and thus applicable as current-carrying conductors. REBCO bulks are also applicable as passive devices coupled with normal permanent magnets. In LN_2, bulk superconductors exert a large repulsive force against a permanent magnet due to a magnetic field generated by the shielding currents when the magnet is approached. Superconducting bulks also exert an attractive force due to the pinned(or trapped) magnetic flux within bulks when the magnet is detached, which enables a stable levitation of the magnet on the top of the bulks. In addition, as shown in Fig. 6 and Fig. 7, superconducting bulks can trap very high fields, these are applicable as active devices.


Effect of the J_c on the trapped field for the identical sample dimension

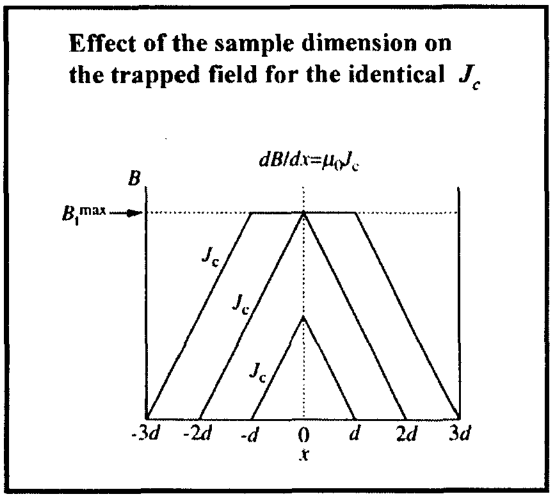

Effect of the sample dimension on the trapped field for the identical J_c

Fig. 8. Schematic illustration of the trapped field distribution representing the effects of J_c (top) and sample dimension (bottom) [12].

Two important factors for bulk applications are J_c and the size of the single domain. Since the repulsive force linearly increases with increasing J_c and the supercurrent loop size, larger repulsive forces are obtainable from higher J_c and larger single-domained REBCO bulks. Similarly, the trapped field capability also depends on J_c and the sample dimension of the REBCO single domain, which are schematically illustrated in Fig. 8. In this figure, the simple Bean model was assumed. Upper limit of the trapped field is bounded by the irreversibility field at a given temperature.

Various bulk applications are under development. As current-carrying conductors, bulk HTS are applicable to current leads and fault current limiters, which are mainly under progress by European countries. As passive devices, superconducting bulks are applicable for the levitators of the wheel in the flywheel energy storage systems. 10 kWh-class flywheel systems have been constructed and tested in USA and Japan. Higher electric power systems are under developmet. Bulk applications as active devices include the magnetic field source, DC motors, and magnetic separation system. Among these applications, the magnetic separation system as shown in Fig. 9 will be commercialized soon in Japan. This system utilizes a steep gradient of the trapped field in the bulk superconducting magnet. Since stronger REBCO bulk magnets can be used instead of normal metallic permanent magnets, more applications as active devices are expected in future.

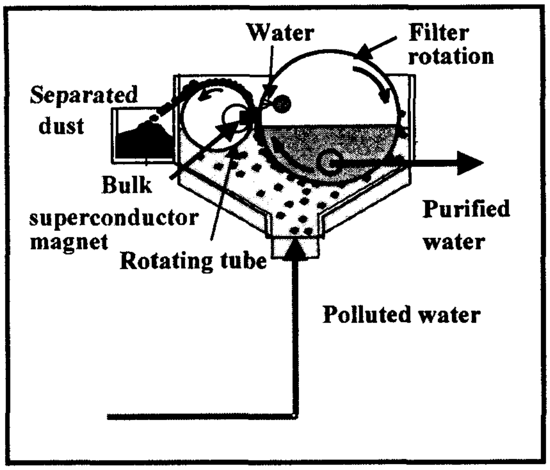


Fig. 9. Schematic illustration of Magnetic separation system(data from ref. [13]). Polluted water can be purified by the magnetic separation using a REBCO bulk superconducting magnet.

IV. Summary

The field of bulk HTS superconductors has been greatly advanced and thus efforts for various bulk applications of REBCO superconductors are under progress. While YBCO bulks have already been commercialized, LREBCO bulks, very promising as active devices, have not been fully developed yet. Further improvement of J_c at 77 K may be obtainable if the average particle size of the second phase trapped in the RE123 superconducting matrix are refined to a nanometer scale. Enhancement of mechanical properties of REBCO bulks will become more critical issue for bulk applications as active devices. Some applications like the magnetic separation system will be commercialized soon.

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