

# Trapped Field Performance of the $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$ Bulk Superconductors Fabricated by Cooling-Rate-Control-Melt-Growth

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**Abstract.** For  $\text{LRE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  (LRE: Light rare-earth superconductors, e.g., Nd, Sm and Gd), cation off-stoichiometry caused by the substitution of  $\text{LRE}^{3+}/\text{Ba}^{2+}$  degrades their superconducting properties. Cooling-Rate-Control-Melt-Growth (CRCMG) method is an effective approach to suppress the substitution of RE element on Ba sites. To investigate the relationship between the cooling rate and trapped field performance in  $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  bulk, we fabricated some full-growth  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks with different second-stage cooling rates (0.1, 0.3, 0.5, 0.8, and 1.0 °C/h) by the CRCMG method, and studied the correlation of the cooling rate and the trapped flux of these bulks. From the results, we found that the maximum trapped flux density and the trapped flux of all bulks have few difference at liquid nitrogen temperature, which indicates that the cooling rate seems to affect insignificantly the trapped flux property of  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks.

## 1. Introduction

Due to its high flux-trapping capability,  $\text{RE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulk superconductors are attractive in industrial power applications such as motors [1, 2].  $\text{RE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  superconductors have high superconducting transition temperature ( $T_c$ ) and high flux-trapping capability. Particularly,  $\text{LRE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  superconductors could exhibit higher  $T_c$  and larger critical current density ( $J_c$ ) than the other  $\text{RE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  superconductors. For example,  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  have been reported to trap a magnetic field of 3 T at 77 K [3]. However, due to the  $\text{LRE}^{3+}$  and  $\text{Ba}^{2+}$  ionic radius are similar, the substitution of  $\text{LRE}^{3+}$  element on  $\text{Ba}^{2+}$  sites easily occurs. And cation off-stoichiometry caused by this substitution might lead to lower  $T_c$  and degrades the performance of bulk, which is common in air-processed  $\text{LRE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulk. Therefore, we need to control the  $\text{LRE}^{3+}/\text{Ba}^{2+}$  substitution for bulk applications.

Previous studies have shown that when the  $\text{LRE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulk are prepared in a reduced oxygen atmosphere, the substitution of  $\text{Ba}^{2+}$  site by  $\text{LRE}^{3+}$  ion was significantly reduced (the so-called Oxygen-Control-Melt-Growth OCMG) [4, 5]. On the other hand, Composition-Control-Melt-Growth (CCMG) method also can suppress  $\text{LRE}^{3+}/\text{Ba}^{2+}$  substitution [6, 7]. Recently, it has been reported that



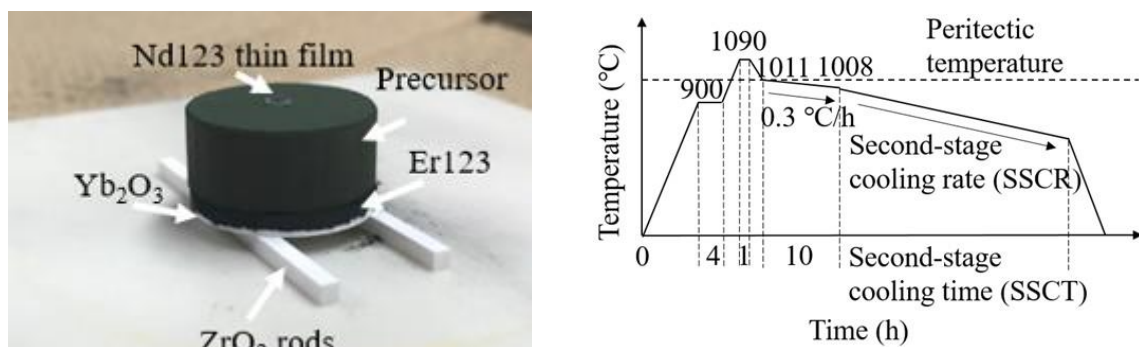
the Cooling-Rate-Control-Melt-Growth (CRCMG) method could effectively control the cation stoichiometry for air-processed  $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulk, gaining a comparable  $T_c$  to those from OCMG and CCMG [8]. To further study on the advantages of the CRCMG method, we fabricated several  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks by the CRCMG method, using a variety of second-stage cooling rate (SSCR) during the growth of these bulks as 0.1, 0.3, 0.5, 0.8, and 1.0 °C/h. Finally, we conducted field-cooled magnetization of these bulks to clarify the relationship between the cooling rate and the trapped field.

## 2. Experimental

We prepared  $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Gd123) starting powder by calcining commercial  $\text{Gd}_2\text{O}_3$ ,  $\text{BaO}_2$  and  $\text{CuO}$  at 920 °C for 24 h and repeated for two times. Commercially available  $\text{Gd}_2\text{BaCuO}_5$  (Gd211) powders,  $\text{Ag}_2\text{O}$  and  $\text{Pt}$  were used as starting materials. The powders of the  $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and the  $\text{Gd}_2\text{BaCuO}_5$  were mixed in a molar ratio of  $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta} : \text{Gd}_2\text{BaCuO}_5 = 10:3$ . 0.5 wt%  $\text{Pt}$  and 10 wt%  $\text{Ag}_2\text{O}$  were also added to the mixture in order to improve the mechanical property and coarsen  $\text{Gd}_2\text{BaCuO}_5$ . The powders were thoroughly mixed and then uniaxially pressed into a pellet with diameter of 20 mm as a precursor. The precursor used for this process is shown in figure 1(a). The precursor was placed on  $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$  pellet used as a liquid source [9]. The commercial Nd123/Y123/MgO thin films, a 600 nm Nd123 films with a 25 nm Y123 buffer layer on the MgO substrate, grown by thermal co-evaporation, were provided by the German Company of Ceraco ceramic coating GmbH. A 2 mm×2 mm thin films were placed on the top of the pre-form at the beginning. The assembly was conducted above a thin  $\text{Yb}_2\text{O}_3$  pellet to support the liquid phase, then onto Y-stabilized  $\text{ZrO}_2$  supporting rods inside a conventional box furnace.

The bulk were first heated to 900 °C and kept for 4 h, further heated to 1090 °C and kept for 1 h. Then, the temperature was decreased to 1011 °C, which was the starting temperature of slow cooling stage. All bulks were cooled at a rate of 0.3 °C/h from 1011 °C to 1008 °C; then the bulks were cooled at different second-stage cooling rates of 0.1, 0.3, 0.5, 0.8, and 1.0 °C/h until crystal growth was completed, as shown in figure 1(b) and Table 1. Annealing process was carried out in flowing oxygen at 450 °C to 300 °C for 200 h. After annealing process, height of the bulks was adjusted to 6 mm.

We measured the trapped field of these bulks, which were magnetized by the field-cooled magnetization with a 1 T external magnetic field paralleled to the c-axis at LN2 temperature. Trapped field of



**Figure 1.** (a) Picture of the bulk before melt growth. (b) Heat treatment process of the fabrication of  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks by CRCMG.

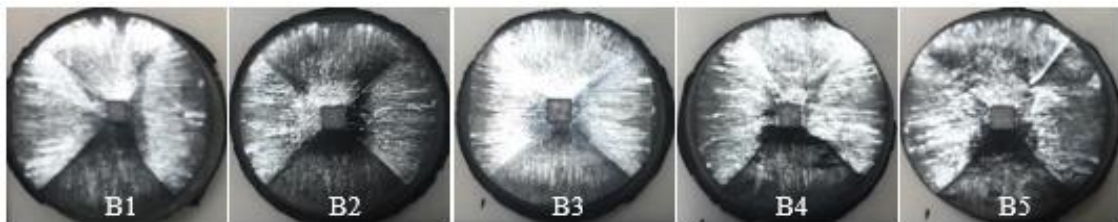
**Table 1.** Growth parameters of  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks.

	SSCR (°C/h)	SSCT (h)
B1	0.1	50
B2	0.3	30
B3	0.5	30
B4	0.8	25
B5	1.0	20

each bulk was measured 15 minutes later after the magnetization by an automatic Hall probe scanning system (sensor: F. W. Bell, BHT-921) [1-3]. The sensor was located 0.5 mm above the surface of the bulks. The sampling interval is 1 mm during trapped field measurement.

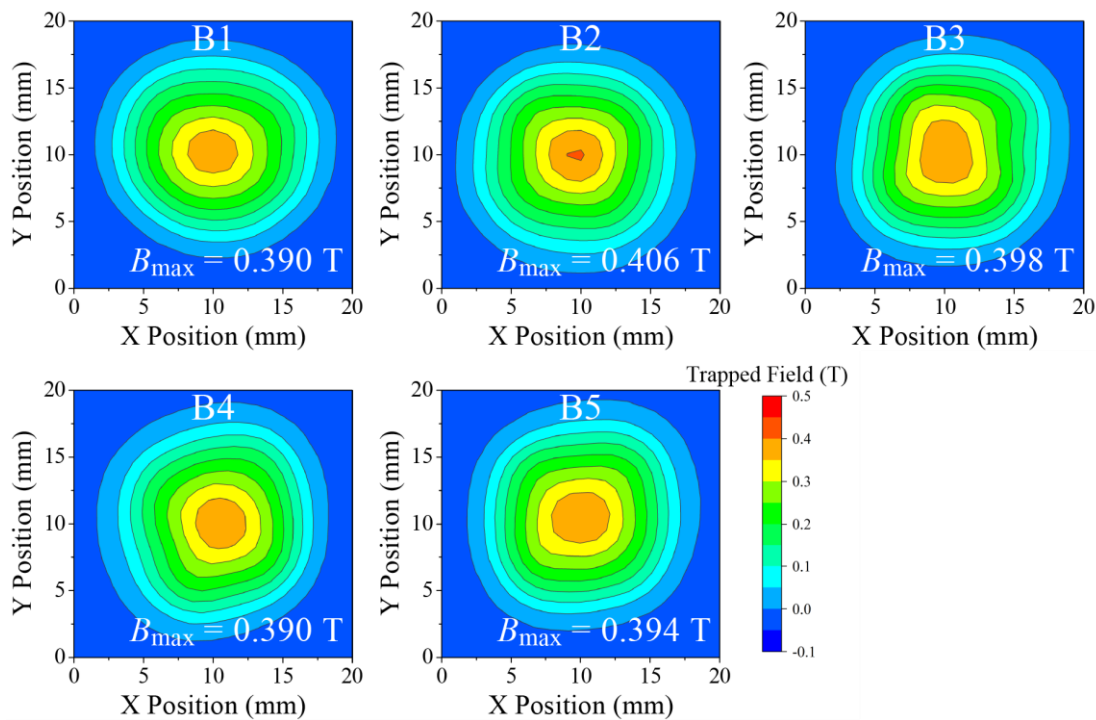
### 3. Results and discussion

The top surface view of  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks with diameter of 16 mm is shown in Figure 2. From these pictures, we found that all the bulks have no self-nucleation. Full-growth  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks were successfully prepared with the different second-stage cooling rates by the CRCMG method. The trapped flux density distributions of each bulk are displayed in Figure 3. We observed that all the bulks have single growth domains, which indicates the bulks have no remarkable weak links.



**Figure 2.** Top view of  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks B1, B2, B3, B4 and B5 grown with different second-stage cooling rates 0.1, 0.3, 0.5, 0.8 and 1.0 °C/h, respectively.

From Table 2, we observed the maximum values of trapped flux density at liquid nitrogen temperature is 0.390 T, 0.406 T, 0.398 T, 0.390 T, and 0.394 T for B1, B2, B3, B4, and B5, respectively. And the maximum trapped flux density reaches 0.406 T for B2. The lowest maximum trapped flux density is 0.390 T for B4.



**Figure 3.** The corresponding trapped flux density distribution of  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks B1, B2, B3, B4 and B5 with different cooling rates 0.1, 0.3, 0.5, 0.8, and 1.0 °C/h at liquid nitrogen temperature.

The maximum trapped field of B2 increases by 4% compared with that of B4. These results, demonstrate that the maximum trapped flux density of the  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks prepared with different second-stage cooling rates from 0.1 °C/h to 1.0 °C/h does not evidently change. The maximum integrated trapped flux reaches 35.7  $\mu\text{Wb}$  for B3. The minimum integrated trapped flux is 32.2  $\mu\text{Wb}$  for B1. The maximum integrated trapped flux increases by 11 % compared with the minimum one.

**Table 2.** The maximum trapped field density and integrated trapped field of  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks with different second-stage cooling rates (SSCR).

	SSCR (°C/h)	Maximum trapped flux density (T)	Integrated trapped flux ( $\mu\text{Wb}$ )
B1	0.1	0.390	32.2
B2	0.3	0.406	33.7
B3	0.5	0.398	35.7
B4	0.8	0.390	32.2
B5	1.0	0.394	35.0

It indicates that the different second-stage cooling rates do not provide obvious influence on the integrated trapped flux of the bulks, which is consistent with the results of the trapped flux density. As illustrated above, the different second-stage cooling rates from 0.1 °C/h to 1.0 °C/h do not affect the trapped field performance of the  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks.

Almost the same trapped flux property was observed regardless of different fabrication process with the different second-stage cooling rates. We think that considerable homogeneity has been achieved according to the sample preparation in which  $\text{ErBa}_2\text{Cu}_3\text{O}_{7-\delta}$  pellet employed as a liquid source [9]. One of the reasons may come from a smaller range of  $\text{Gd}^{3+}/\text{Ba}^{2+}$  substitution in  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  than in  $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  since the  $\text{Gd}^{3+}$  ion is smaller than  $\text{Sm}^{3+}$  or  $\text{Nd}^{3+}$  ions [3]. The maximum substitution content in the  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  is  $x = 0.1$  [10]. This value is small compared with that of other  $\text{LRE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  superconductors. As a result, the trapped field performance of  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulk is not remarkably changed by alternating the second-stage cooling rate.

#### 4. Conclusion

We succeeded in preparing five full-growth  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks with different second-stage cooling rates 0.1, 0.3, 0.5, 0.8, and 1.0 °C/h using the CRCMG method. Almost the same trapped field performance was observed regardless of different fabrication process with the different second-stage cooling rates. As a result, it is suggested that second-stage cooling rates from 0.1 °C/h to 1.0 °C/h do not influence the trapped flux of  $\text{Gd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$  bulks. Further study will be carried out to clarify  $J_c$ - $B$  characteristics,  $T_c$ , and lattice parameters on the samples with approval of homogeneity.

#### References

- [1] Miki M, Felder B, Tsuzuki K, Xu Y, Deng Z, Izumi M, Hayakawa H, Morita M and Teshima H 2010 *Supercond. Sci. Technol.* **23** 124001
- [2] Zhang Y, Zhou D, Ida T, Miki M and Izumi M 2016 *Supercond. Sci. Technol.* **29** 044005
- [3] Nariki S, Sakai N and Murakami M 2005 *Supercond. Sci. Technol.* **18** S126
- [4] Sakai N, Yoo S.I, Watahiki M, Higuchi and Murakami M 1995 *Adv. Supercond.* **VII** 345
- [5] Oda M, Yao X, Yoshida Y and Ikuta H 2009 *Supercond. Sci. Technol.* **22** 075012
- [6] Cardwell D.A, Shi Y, Hari Babu N and Iida K 2009 *Phys. C supercond.* **469** 1146
- [7] Dai J.Q, Zhao Z.Q and Xiong J.W 2003 *Supercond. Sci. Technol.* **16** 815
- [8] Cui X.X, Wang W, Zhuang Y.F, Guo L.S, Xiang H.Yao X, Pan B, Ikuta H and Zou Z.Q 2016 *J. Alloys Comp.* **663** 10
- [9] Zhou D, Hara S, Li B, Noudem J and Izumi M 2014 *Supercond. Sci. Technol.* **27** 7
- [10] Xu C, Hu A, Sakai N, Izumi M and Hirabayashi I 2005 *Phys. C supercond.* **417** 77