pISSN 1229-3008 eISSN 2287-6251
Progress in Superconductivity and Cryogenics
Vol.24, No.3, (2022), pp.35~40 https://doi.org/10.9714/psac.2022.24.3.035

Fabrication of a large grain YBCO bulk superconductor by homo-seeding melt growth method

Hee-Gyoun Lee*

Tech University of Korea, Siheung, Korea

(Received 26 July 2022; revised or reviewed 15 September 2022; accepted 16 September 2022)

Abstract

To fabricate large grain YBCO bulk superconductors by melt process, Sm123 single crystal with a high melting point are mostly used as seeds. However, it also uses Y123 film deposited on MgO single crystal substrate. This study investigated the growth behavior of the Y123 grain during a melt process when single grain YBCO bulk was used as a seed. Single grain Y123 bulk was grown when the seed size was small. When the seed size was relatively large, multiple grains were grown but the grains were still large. Y123 seed crystal was completely decomposed during high temperature anneal at 1040℃ and new Y123 crystals were nucleated during a slow cooling stage below a peritectic temperature. Thereafter, newly formed Y123 crystals from the seed area are thought to grow into the Y1.8 powder compact. The crystallographic orientations of newly nucleated Y123 grains are independent of the crystallographic orientation of Y123 seed. It is thought that the crystallographic orientation of newly nucleated Y123 crystal can be controlled by using Y211-free Y123 single crystal as a seed of homo-seeding melt growth.

Keywords: YBCO, bulk superconductors, Y211, homo-seeding, melt process

1. INTRODUCTION

Single grain $REBa_2Cu_3O_{7-y}$ (RE123, RE: rare-earth elements) bulk superconductors have a great potential for the applications of magnetically levitated system, permanent magnets, magnetic shielding, and so on [1, 2]. The large grain YBCO bulk superconductors have been fabricated by a top-seeded melt growth (TSMG) or by a top-seeded infiltration growth (TSIG) process [3-8]. Seed crystals are selected among the REBCO single crystals having higher melting point than the processing material. In case of fabricating single grain Y123 bulk superconductor, Sm123 single crystal with embedded Sm211 crystals are usually used as a seed crystal. However, Sm123 seed is partially dissolved during a melt process [9] and deteriorates the superconducting properties of the melt-processed Y123 bulk superconductor [10].

Scruggs et al. [11] successfully fabricated a high magnetization single grain Y123 bulk superconductor using Y123 single crystal seed (hereafter, homo-seed) by a hot seeding method that Y123 seed was put onto the quisi-melted Y1.8 powder compact below a peritectic temperature after the high temperature anneal at 1040℃. Y123 film deposited on single crystal MgO substrate also was used as the seed for the preparation of single grain YBCO bulk material [12-13]. It has been reported that the YBCO film on a MgO substrate is only partially up to dissolved partially even at extremely high temperature of 1170℃ and is thought to act as a seed for the growth of Y123 crystal [12]. However, it is thought that the Y123 film should be dissolved completely by the heat treatment at 1040 for 2 hours in the presence of BaCuO melt. For the preparation of Y123 film by liquid phase epitaxy (LPE) method, the Y123 film seed are also used. It was reported that Y123 film was partially melted and MgO substrate is exposed to the BaCuO melt even by a short period immersion in the BaCuO melt [15].

This study presents the growth behavior of Y123 crystal grown by homo-seeing melt growth (HSMG) method that Y123 crystal is used as a seed for the fabrication of single grain Y123 bulk material. Single grain Y1.8 bulk crystal was prepared by a conventional TSMG method by using Sm1.8 crystal as a seed. Growth behavior of Y123 crystal was also observed during a seed-free melt growth process. Seed-free melt growth was conducted for the Y1.8 powder compact as well as a single grain Y1.8 bulk after removing the Sm1.8 seed crystal. The effect of the size of seed crystal on the growth behavior of Y123 crystal was investigated for the HSMG of Y1.8 powder compact.

2. EXPERIMENTALS

Precursor powder was prepared by using high purity powders of Y_2O_3, $BaCO_3$, CuO and CeO_2. Nominal composition of the precursor was Y: Ba: Cu = 1.8: 2.4: 3.4 and 1 wt. % CeO_2 was added as a refiner of Y211 particles. Powder mixture was calcined and ground repeatedly and was mixed with 1 wt. % CeO_2 (hereafter, Y1.8).

An appropriate amount of Y1.8 powder was put into a

* Corresponding author: hglee@tukorea.ac.kr

steel mold with a diameter of 30 mm or 40 mm. Compacts were prepared by a uni-axial pressing.

For TSMG, Y1.8 powder compact was placed on the Yb_2O_3 pieces and then a small-sized Sm-123 seed was put on the top surface of the Y1.8 pellet at last. The heat treatment procedure for melt growth (MG) was like those reported in the literature [6]. The cooling rate was controlled with 0.4℃h^{-1} at the temperature regime for the growth of Y123 grains. After the MG heat treatment, Y1.8 samples were heated to 500℃ at a rate of 200℃h^{-1} in flowing oxygen for oxygenation, held at this temperature for 50 h, cooled to 400–500℃ at a rate of 100℃h^{-1}, held at this temperature for 200-300 h, and then cooled to room temperature at a rate of 200℃h^{-1}.

For the HSMG experiment, the seed crystals with various sizes were prepared by slicing a large single grain Y1.8 bulk specimen. To investigate the nucleation behavior in a melt processed YBCO grain, the seed-free melt growth has been conducted again for Y1.8 powder compact as well as for a large single grain Y1.8 bulk. Seed-free melt growth for a large single grain Y1.8 bulk was conducted after grinding the top surface and cut along <100> axis and/or <010> axis to know the change of crystallographic orientations of the Y123 crystals after the melt process.

The microstructures of the melt-processed specimen were investigated using an optical microscope (OP).

3. RESULTS AND DISCUSSION

Figure 1 shows the top views of the bulk specimens which were prepared by a TSMG and a seed-free melt growth of Y1.8 powder compact. It is seen that single grain Y1.8 bulk was grown with well-defined <110> facet lines by TSMG while multiple grains were formed by a seed-free melt growth process. From the observation of crack directions, it can be said that crystallographic orientations of the multiple grains are random.

Figure 2 shows the result that the seed-free melt growth has been applied for a large single grain Y1.8 bulk. To compare crystallographic orientations of the Y123 crystals before and after the melt process, Top surface of the single grain Y1.8 bulk was polished after removing a Sm123 seed and cut along <100> axis and/or <010> axis. Compared to seed-free melt growth of Y1.8 powder compact, only limited number of grains were grown for the single grain Y1.8 bulk specimen. It means that only limited number of Y123 nuclei were formed and grow fast.

Melt growth process of REBCO system, RE123 crystals are grown in the mixture Y211 + BaCuO melt irrespective of the presence of a seed crystal. In case of the seed-free melt growth, Y123 crystal should be nucleated form the mixture of Y211 + BaCuO melt. It can be said that Y123 crystals are nucleated heterogeneously on Y211 crystal because the critical Gibbs free energy for heterogeneous nucleation is much smaller than that of homogeneous nucleation. Y211 crystals are formed during a calcination process as well as by the decomposition of the randomly oriented Y123 crystals during a ramping step to high temperature during a melt process. Therefore, the

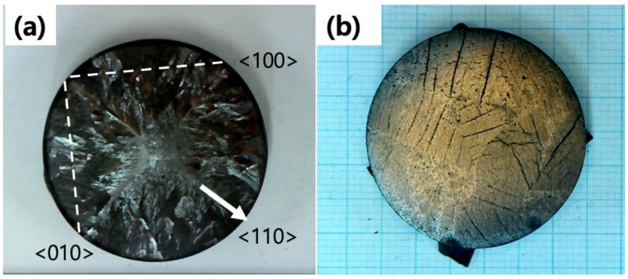

Fig. 1. Top-views of the Y1.8 bulks fabricated by a melt process (a) with Sm1.8 single crystal seed and (b) without a seed, respectively. Specimens were polised to reveal the cracks between (001) planes generated during oxygenation heat treatment.

crystallographic orientation of Y123 crystals, which were nucleated from Y211 crystal heterogeneously, should be arbitrary because the crystallographic orientations of the Y211 crystals are random.

Yellow dotted circle presents the location where Sm123 seed was placed during TSMG process. White-colored dotted line, which denotes the boundary between grain 1 and grain 3, is parallel to <100> or <010> directions because it is coincided with the direction of the cracks during the oxygenation process. Red-colored arrows presents the facet lines that have formed during the growth of Y123 crystal along <110> direction.

By comparing the Fig. 2(a) and Fig. 2(b), <100> or <010> direction was rotated about 23° normal to surface after a seed-free melt growth. Angle between <110> facet lines is measured as 70°. Therefore, it is thought that newly grown Y123 crystals have no special orientation relationship with starting crystallographic orientation of the Y123 crystal before the melt process. It can be mentioned that starting Y1.8 bulk was completely decomposed during the high temperature anneal at 1040℃ for 2 hours and newly grown Y123 grains in Fig. 2(b) were nucleated heterogeneously from Y211 + BaCuO melt. Side-views of the specimen (denoted as arrow A and B in Fig. 2(b)) are shown in Fig. 2(c) and Fig. 2(d). From the observations of side-views, it is also seen that multiple grains are formed with various crystallographic orientations.

Figure 3 shows a schematic drawing of BSMG process [16] and the top-view of the Y1.8 specimen which was prepared by a BSMG method. In previous seed-free experiment, multiple grains were formed but the grain size of the bottom-seeded specimen are much smaller than that in Fig. 2(b) and rather similar with the grain size of the specimen in Fig. 1(b). It means that, for BSMG, single grain Y1.8 bulk might not act as the preferential nucleation sites of Y123 crystals or the Y1.8 green pellet might influence on the nucleation and growth behavior of single grain Y1.8 bulk.

Cai et al. suggested that the increase of the effective seeding dimension decreases the opportunities of multiple nucleation [17, 18]. It infers that the size of Y1.8 homo-seed may give influence on the nucleation behavior in Y211 + BaCuO melt mixture formed from Y1.8 homo-seed. In other words, the number of nuclei is dependent on the

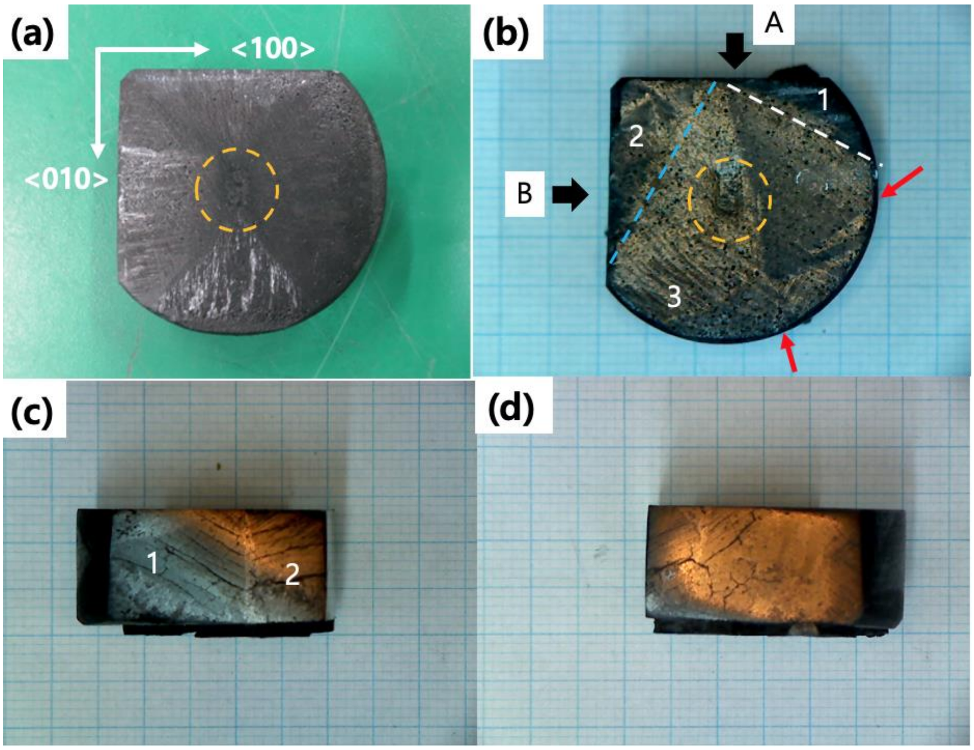

Fig. 2. Top-views and side-views of the Y1.8 bulk specimens. (a) Y1.8 bulk prepared by TSMG using Sm1.8 seed, (b) Y1.8 bulk prepared by a seed-free melt growth using the Y1.8 bulk of fig. 2(a), (c) side-view from A side and (d) side-view from B side.

effective seeding dimension. If the effective seeding dimension is D_{eff}, then it may be possible to get a single grain Y123 bulk by using a Y1.8 seed with a smaller dimension than D_{eff}.

Based on the seed-free experiments and BSMG using single grain Y1.8 bulk, following assumptions have been made. (1) In the seed-free melt growth, the effective seeding dimension of single grain Y1.8 bulk is larger than that of Y1.8 powder compact. (2) In the seed-free melt growth, newly formed nuclei have no crystallographic orientation relationship with the crystallographic orientation of starting single grain Y1.8 bulk. (3) If the effective seeding dimension is D_{eff}, then it may be possible to get a single grain Y123 bulk by using Y1.8 homo-seed with a smaller dimension than D_{eff}.

Based on the above assumptions, HSMG was carried out by using the single grain Y1.8 seeds with different dimensions of about 15 x 15 x 5 mm^3 and about 4 x 4 x 2 mm^3. Side of seed are parallel to <100> or <010> direction of Y123 crystal and the surface of seed is normal to <001> direction of Y123 crystal. Figure 4 shows the top-views and the cross-sectional-views of the Y1.8 bulks grown by HSMG method using the single grain Y1.8 homo-seeds with different dimensions. It is seen that large-sized grain are appeared independent of the dimension of single grain Y1.8 homo-seed which was applied as a top-seed. However, large single grain was grown in the case that small seed with a dimension of about 4 x 4 x 2 mm^3 was used while multiple grains were formed for the specimen with large seed dimension of about 15 x 15 x 5 mm^3. As mentioned previously, melt growth includes high temperature anneal at 1040℃ for 2hours. Therefore, the

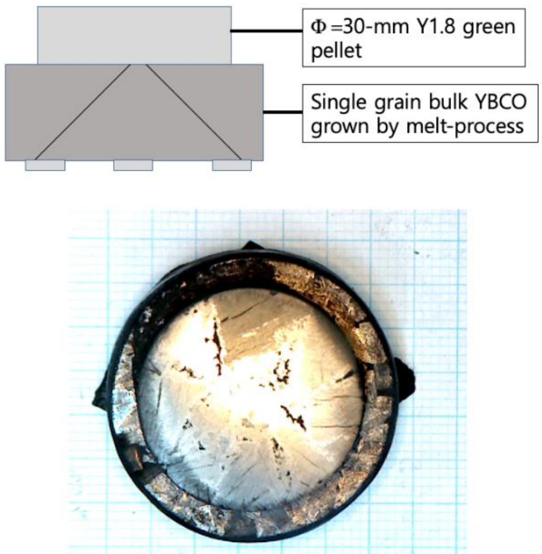

Fig. 3. Schematic drawing and the top-view of bottom-seeded melt grown Y1.8 bulk specimen.

grains in Fig. 4 might be newly nucleated and grown as large grains like TSMG where Sm123 hetero-seed is applied.

Figure 5 shows the microstructures of the Y1.8 homo-seed crystals before HSMG and after HSMG, respectively. Figure 5(a) and fig. 5(b) are the microstructures before HSMG and fig. 5(c) and fig. 5(d) are the microstructures after HSMG. It is seen that, in Y1.8 homo-seed before HSMG, Y211 crystal are randomly distributed with the size of about 5-20 μm. Obviously, the microstructures

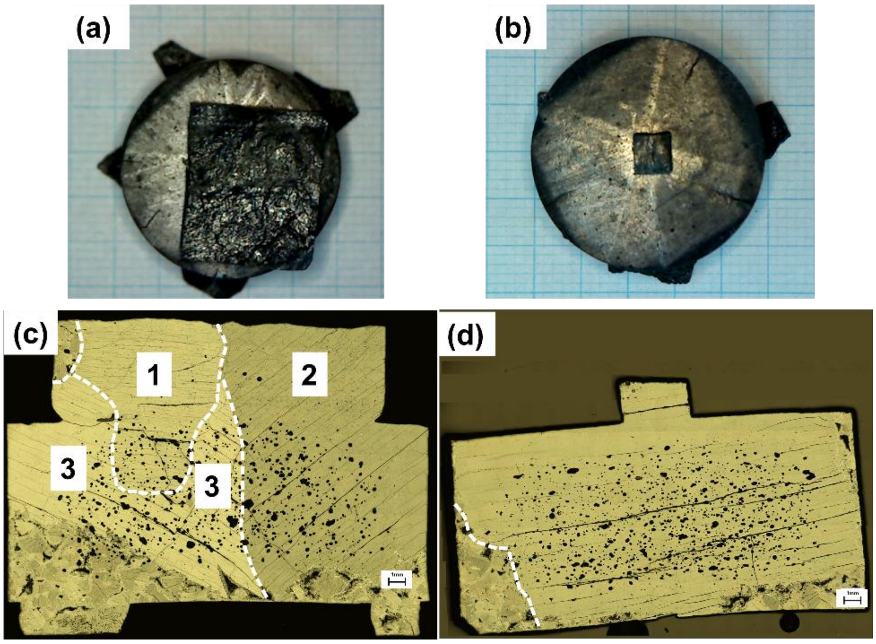

Fig. 4. Top-views and side-views of Y1.8 bulk prepared by HSMG method using Y1.8 crystal as the seeds. Seed dimension was about 15 x 15 x 5 mm3 for (a), (c) and about 4 x 4 x 2 mm3 for (b), (d), respectively.

before HSMG are nearly the same independent of the seed dimension because both seeds are prepared by the same process and the same powder. However, microstructures are clearly distinguished depending on the seed dimension even though the same Y1.8 powder compact and the same Y1.8 homo-seed were used. For the specimen with a small dimension Y1.8 homo-seed, the size and the distribution of Y211 crystal do not show noticeable changes. However, for the specimen with a large dimension seed, there is no noticeable change of large-sized Y211 crystals of about 20 μm but a plenty of small-sized Y211 crystal of about 1 μm is newly observed.

Figure 6 shows the microstructures near the boundary between Y1.8 homo-seed and Y1.8 powder compact after HSMG process. The size and the distribution of Y211 crystal are similar for both specimens independent of the seed dimension in the sections of Y1.8 powder compact. Therefore, for the specimen with small-sized seed, the size and distribution of Y211 crystal were not much different across the seed/Y1.8 powder compact boundary. However, for the specimen with large-sized seed, two areas of Y1.8 homo-seed and Y1.8 powder compact are clearly distinguished.

From the observations of microstructures and grain growth behaviors, followings are discussed. (1) For the specimen of small-sized Y1.8 homo-seed, small-sized Y211 crystal might be ripened by the large-sized Y211 crystal in the melt which might be supplied from the Y1.8 powder compact. (2) For the specimen of small-sized Y1.8 homo-seed, the grain growth inhibition force might be small because the size of Y211 crystal is large. Therefore, Y123 grain may grow fast due to a relatively weak inhibition force. (3) For the specimen of large-sized Y1.8 homo-seed, the melt effect from bottom Y1.8 powder compact is small because the seed volume is big resulting in long diffusion length. (4) Small-sized Y211 crystals of about 1 μm might be generated via a decomposition of Y1.8 homo-seed because they were not present in Y1.8 homo-seed before HSMG. (5) small-sized Y211 crystals might act as strong grain growth inhibitor and lower the growth rate of Y123 crystal. (6) For the specimen of large-sized Y1.8 homo-seed, the effective seeding dimension is decreased with slow growth rate and then the opportunities of multiple nucleation are increased.

Single grain Y1.8 bulk has been successfully fabricated by using a combination of HSMG and cold-seeding method. However, Y1.8 crystal seed includes pre-existing Y211 crystal and therefore grown Y123 crystals have random crystallographic orientation. Haugan et al. [19] reported that the lattice mismatch of Y211 with respect to Y123 is of the order of 2%–7%, depending on the growth orientation of Y211 with respect to Y123. Hu et al. observed the epitaxial decomposition of Y211 crystal from Y123 film on MgO substrate [17, 18] and also reported the epitaxial nucleation of RE123 crystal from Sm211 crystal [20]. From the above reports, it may be possible to assume that Y211 crystals is decomposed epitaxially from Y211-free Y123 single crystal during a ramping step of melt growth and well-defined Y211 crystals can act as epitaxial nucleation sites of Y123 crystal. If Y211-free Y123 crystal is used as a seed of HSMG, it may be possible to fabricate the single grain Y1.8 bulk specimen with a controlled crystallographic orientation by HSMG method. Homo-seeding is clearly beneficial for the fabrication of contamination-free high quality Y123 bulk superconductor by eliminating Sm123 hetero-seed.

4. CONCLUSIONS

Summarizingly, single grain Y123 bulk has been fabricated by using Y1.8 homo-seed for HSMG method.

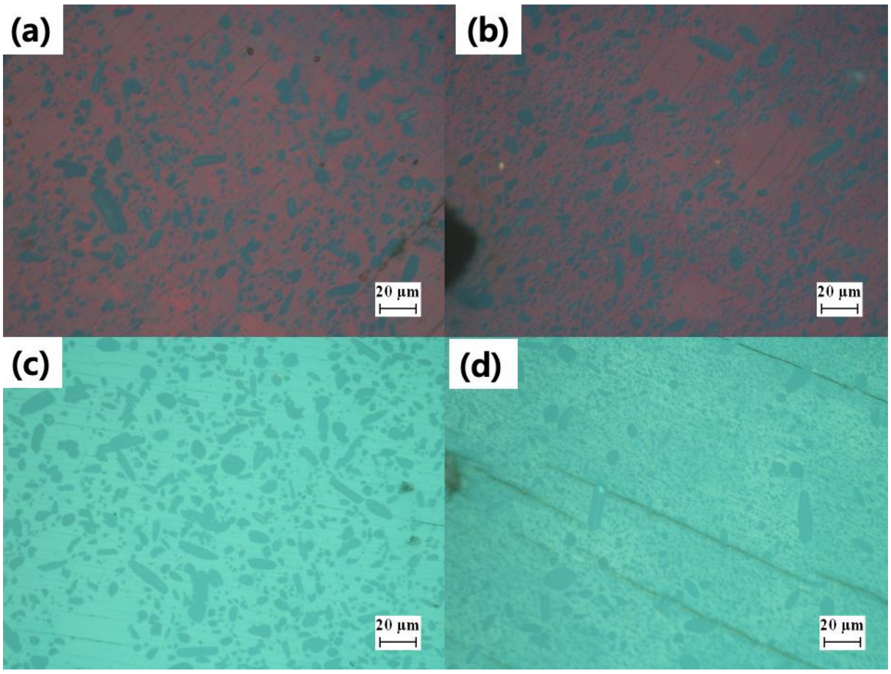

Fig. 5. Microstructures of Y1.8 seed crystal before(a,b) and after(c,d) HSMG. Seed dimension was about 15 x 15 x 5 mm3 for (a), (c) and about 4 x 4 x 2 mm3 for (b), (d), respectively.

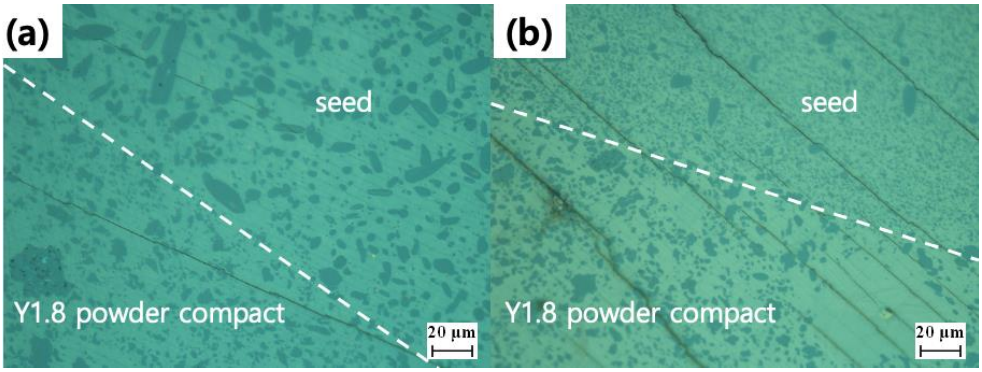

Fig. 6. Microstructures near the Y1.8 seed/Y1.8 powder compact boundaries. (a) the specimen with a small dimension seed and (b) the specimen with a large d1mension seed. Dotted lines denote the boundaries between the Y1.8 seed and the Y1.8 powder compact.

Y1.8 homo-seed itself does not act as a seed of melt growth because Y1.8 homo-seed is completely decomposed into Y211 + BaCuO melt mixture. Depending on the size of Y1.8 homo-seed, the growth behavior is changed. Multiple grains are nucleated when the size of Y1.8 homo-seed is bigger than the effective seeding volume. The crystallographic orientations of newly nucleated Y123 grains are independent of the crystallographic orientation of Y123 seed. It is thought that the crystallographic orientation of newly nucleated Y123 crystal can be controlled by using Y211-free Y123 single crystal as a seed of homo-seeding melt growth.

ACKNOWLEDGMENT

This work has been conducted by using the research facilities of Korea Atomic Energy Research Institute.

REFERENCES

[1] M. Murakami, “Processing and Applications of Bulk RE–Ba–Cu–O Superconductors”, *Int. J. Appl. Ceram. Technol*., 4 [3], pp. 225–241, 2007

[2] J. H Durrell, M. D Ainslie, D. Zhou, P. Vanderbemden, T. Bradshaw, S. Speller, Filipenko and D. A Cardwell, “Bulk superconductors-a roadmap to applications”, *Supercond. Sci. Technol*., 31, 103501, pp.17, 2018

[3] M. Morita, S. Takebayashi, M. Tanaka, K. Kimura, K. Miyamoto, and K. Sawano “Quench and melt growth (QMG) process for large bulk superconductor fabrication, “*Adv. Supercond*. Vol. 3, pp. 733-736, 1991.

[4] S. Meslin and J. G. Noudem, “Infiltration and top seeded grown mono-domain $YBa_2Cu_3O_{7-x}$ bulk superconductor,” *Supercond. Sci. Technol*., vo.l.17, pp.1324-1328, 2004

[5] P. Schaetzle, G. Krabbes, G. Stover, G. Fuchs, D. Schlafer, “Multi-seeded melt crystallization of YBCO bulk material for cryogenic applications, “*Supercond. Sci. Technol*. vol. 12, pp. 69–76, 1999.

[6] Y.A. Jee, C.-J. Kim, T.-H. Sung, G.-W. Hong, “Top-seeded melt growth of Y-Ba-Cu-O superconductor with multi-seeding, “*Supercond. Sci. Technol*. vol. 13, pp. 195-201, 2000.

[7] C-J Kim, Jee YA Jee, SC Kwon, TH Sung, GW Hong “Control of YBCO growth at the compact/substrate interface by bottom seeding

and Yb_2O_3 coating in seeded melt-growth processed YBCO oxides using a MgO substrate, "*Physica C*, vol. 315, pp. 263-270, 1999.
[8] A. Goodfellow, Y-H. Shi, J.H. Durrell, A.R. Dennis, D.A. Cardwell, C.R.M. Grovenor and S.C. Speller, "Microstructural evolution in multi-seeded YBCO bulk samples grown by the TSMG process." *Supercond. Sci. Technol.* 29, pp115005-115015, 2016
[9] Y.A. Jee, G.W. Hong, C.J. Kim and T.H. Sung, "Dissolution of $SmBa_2Cu_3O_{7-y}$ seed crystals during top-seeded melt growth of $YBa_2Cu_3O_{7-y}$" , *Supercond. Sci. Technol.* ,11, 650-658, 1998
[10] C.D. Dewhurst, W. Lo, Y.H. Shi and D.A. Cardwell, "Homogeneity of superconducting properties in -seeded melt processed YBCO", *Mater. Sci. Eng*., 53, pp. 169-173, 1998
[11] S.J. Scruggs, P.T. Putman, Y.X. Zhou, H. Fang and K. Salama, "Hot seeding using large Y-123 seeds", *Supercond. Sci. Technol.* ,19, S451-S454, 2006
[12] H. H. Xu, L. Cheng, S. B. Yan, D. J. Yu, L. S. Guo and X. Yao, "Recycling failed bulk YBCO superconductors using the NdBCO/YBCO/MgO film-seeded top-seeded melt growth method", J. Appl. Phys. 111, pp. 103910-4, 2012
[13] J. Hu, X. Yao and Q.L. Rao, "Real-time observation of the melting process of YBCO thin film on MgO substrate", *J. Phys.: Condens Matter*, 15, pp. 7149-7154, 2003
[14] Y. Chen, X. Cui, and X. Yao, "Peritectic melting of thin films, superheating and applications in growth of REBCO superconductors," *Progress in Materials Science*, vol. 68, pp. 97–159, 2015
[15] K. Nomura, S. Hoshi, X. Yao, Y. Nakamura, T. Izumi and Y. Shiohara, "Growth mechanism of RE-Ba-Cu-O film on MgO substrate by liquid phase epitaxy", *Physica C*, 357-360, pp. 1377-1381, 2001
[16] Y.S. Hong, S.D. Park, C.J. Kim and H.G. Lee, "Fabrication of a high magnetization YBCO bulk superconductor by a bottom-seeded melt growth method" *Progress in Superconductivity and Cryoge*, vol. 21, no. 4, pp. 19-23, 2019
[17] C. Cai, H. Mori, H. Fujimoto, H. Liu, S. Dou, "Crystal growth patterns in MgO seeded $Y_{1.8}B_{a2.4}Cu_{3.4}O_y$/Ag melt-texturing process", *Physica C*, 357-360, pp. 734-737, 2001
[18] C. Cai and H. Fujimoto, "Effects of Nd123/MgO thin film and MgO single-crystal seeds in isothermal solidification of YBaCuO/Ag**"** *J. Mater. Res.* 15, 1742-1748, 2000
[19] T. Haugan, P.N. Barnes, R. Wheeler, F. Melsenkothen, M. Sumption, "Addition of nanoparticle dispersions to enhance flux pinning of the $YBa_2Cu_3O_{7-x}$ superconductor", *Nature*, 430, pp. 867-870, 2004