

A modified TSIG technique for simplifying the fabrication process of single-domain GdBCO bulks with a new kind of liquid source

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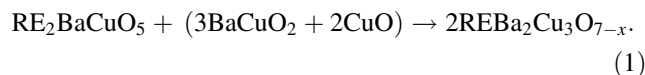
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Abstract The top seeded infiltration and growth process (TSIG) is an effective way for the preparation of bulk $\text{REBa}_2\text{Cu}_3\text{O}_{7-x}$ (RE-123) with finely dispersed $\text{RE}_2\text{BaCuO}_5$ (RE-211) particles compared to the conventional melt growth (MG) method. However, it is more complicated and time-consuming because three kinds of precursor powders, involving RE-211, RE-123, and BaCuO_2 , have to be prepared before the conventional TSIG process. In this article, a new liquid source (NLS) composed of RE_2O_3 (RE-200), BaCuO_2 , and CuO powders, has been found for simplifying the TSIG process, which is different from the regular liquid source (RLS) composed of RE-123 and $\text{Ba}_3\text{Cu}_5\text{O}_8$. In this modified TSIG technique, what we need is only to prepare RE-211 and BaCuO_2 precursor powders for the whole TSIG flow. Single-domain GdBCO bulk superconductors have been fabricated using the RLS and NLS separately. The morphology, microstructure, and levitation force of the GdBCO bulks have also been investigated. The results indicate that the NLS can be used to simplify the process flow, reduce the cost and improve the efficiency on the fabrication of single-domain GdBCO superconductors.

Introduction

Bulk high temperature superconductors, which have significant potential for large-scale engineering applications, have attracted many researchers' attention. It is well known

that top seeded melt growth (TSMG) method is widely used to yield large grain and weak-link free bulk superconductors with high critical current densities (J_c) at 77 K [1, 2]. However, conventional melt processes have some common problems, such as existence of pores and macrocracks, the loss of Ba–Cu–O liquid during peritectic decomposition, heterogeneously dispersed RE-211 particles with various sizes, distortion, and shrinkage of the final samples. In order to overcome these problems, a new technique based on infiltration and growth (IG) has been developed by various laboratories in recent years [3–12]. An important feature of the IG process is that it can be used to fabricate large samples of near-net shape without distortion or macrocracks. Furthermore, the RE-211 inclusions are significantly smaller and distributed homogeneously in the RE-123 matrix even without any addition of CeO_2 or PtO_2 to the precursor powder. Figure 1 schematically shows the generic top seeded infiltration and growth process (TSIG) for fabricating single-domain REBCO superconductors. As shown in the figure, the RE-211 preform bulk was placed on top of the liquid source pellet (a Ba and Cu rich liquid phase) at room temperature firstly, then the liquid phase infiltrated up into the porous RE-211 compact when the sample was heated above the melting temperature of the Ba–Cu–O liquid phase, which then reacted with the RE-211 phase to form RE-123 on cooling, as described by the following reaction:



It can be seen that the Ba and Cu rich liquid phase in a nominal composition of $\text{Ba}_3\text{Cu}_5\text{O}_8$ is just the exact phase needed for reaction with RE-211 phase. But the $\text{Ba}_3\text{Cu}_5\text{O}_8$ (035, i.e., a mixture of BaCuO_2 and CuO powders in a molar ratio of $\text{BaCuO}_2:\text{CuO} = 3:2$) powder cannot solely

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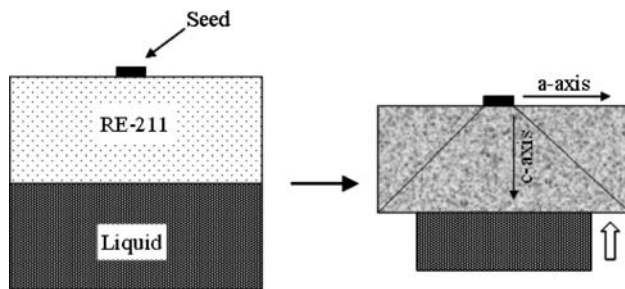
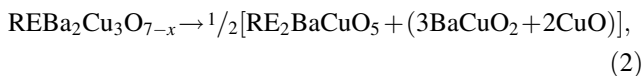


Fig. 1 Schematic illustration of the generic TSIG process for fabricating single-domain REBCO superconductors

be used as liquid source in the configuration shown in Fig. 1, because the $\text{Ba}_3\text{Cu}_5\text{O}_8$ powder will fully melt during the heat treatment process, leading to heavy loss of liquid and collapse of the whole sample. So a mixture of RE-123 and $\text{Ba}_3\text{Cu}_5\text{O}_8$ in a molar ratio of RE-123:035 = 1:1 is commonly used as liquid source for the TSIG process, and the above two cases can be effectively avoided with the support of solid RE-211 particles decomposed from starting RE-123 phase. As a result, three kinds of precursor powders, involving RE-211, RE-123, and BaCuO_2 , have to be prepared before the TSIG process. However, only two kinds of powders containing RE-211 and RE-123 are necessary for conventional MG process. And all the single-phase precursor powders were synthesized initially using the solid state reaction method, by repeated (typically three times) calcinations at 900–960 °C for 24 h and grinding of a stoichiometric mixture of raw RE_2O_3 , BaCO_3 , CuO powders. So it will take about one week to prepare one precursor powder, causing the IG process to be more complicated and time-consuming than the conventional MG process.

In order to simplify the process flow and shorten the experimental cycle, in this article, we demonstrate fabrication of single-domain GdBCO bulks using a new composition of RE-200:CuO: BaCuO_2 = 1:6:10 as liquid source by the TSIG technique. According to the reaction formula:



it is apparent to observe that the atomic ratio in this mixture is just the same as the regular liquid source (RLS) (i.e., RE-123:035 = 1:1), so it is feasible to replace the RLS with this composition as a new kind of liquid source (NLS) for the TSIG process in theory. Furthermore, after this processing, only two types of precursor powders involving RE-211 and BaCuO_2 are needed to prepare for the whole TSIG flow (RE-200 in the NLS is the raw oxide RE_2O_3 , which need not precursory heat treatment), and the RE-123 phase, which is the most difficult to synthesize for its high

hardness after high-temperature calcination, is not present in the precursor powders, thus the experimental efficiency is advanced. Single-domain GdBCO bulk superconductors have been fabricated using the RLS and NLS separately. The morphology, microstructure, and levitation force of the GdBCO products have also been investigated.

Experimental

The powders of Gd-123, Gd_2O_3 , CuO , and BaCuO_2 were weighed according to the molar ratios in RLS and NLS, respectively, then well mixed and ground thoroughly using a ball milling machine for 3–4 h, then the two liquid sources for IG process were obtained. The powders of Gd-211 and liquid source were pressed into pellets of the same diameter 20 mm, respectively. Furthermore, Gd_2O_3 powder was pressed into a plate of thickness 2 mm to support the liquid phase at elevated temperature. Then, the Gd-211 green compact was placed on top of the liquid source pellet, which, in turn, was placed on the liquid support plate. The entire arrangement was then mounted on MgO single crystals, which themselves were placed on an alumina plate. Finally, a well textured NdBCO crystal of dimensions 2 mm × 2 mm × 1 mm was placed on the top surface of the Gd-211 green compact with *ab*-plane parallel to the surface. Then the samples were put in a self-designed tube furnace with appropriate temperature gradient which can effectively prevent the random nucleation of GdBCO grains at the edges of samples [13]. The samples were heated to 800 °C in 8 h, and subsequently up to 1,060 °C in 5 h (a rather low heating rate employed in this stage is for avoiding slope or collapse of the sample due to the rapid melt of BaCuO_2 phase), and held for 1 h to ensure complete infiltration of liquid into Gd-211 preform, cooled to 1,035 °C at a rate of 60 °C/h, and then cooled slowly to 1,015 °C at a rate of 0.2–0.5 °C/h before furnace-cooled to room temperature. After completion of seeded IG process, the single domains were annealed in flowing oxygen for 200 h at temperatures ranging from 450 to 350 °C.

Results and discussion

Figure 2 shows both the top and side view of the GdBCO samples grown using the RLS and NLS by the TSIG technique in air. As we can see from the figure, both the samples exhibit clear, fourfold growth sector boundaries on their top surface, indicating that they are both grown in the form of a single domain. In addition, no spontaneous satellite grains were observed in the samples. As a result, it can be concluded that, difference in liquid source of the samples had little or no effect on the growth rate and

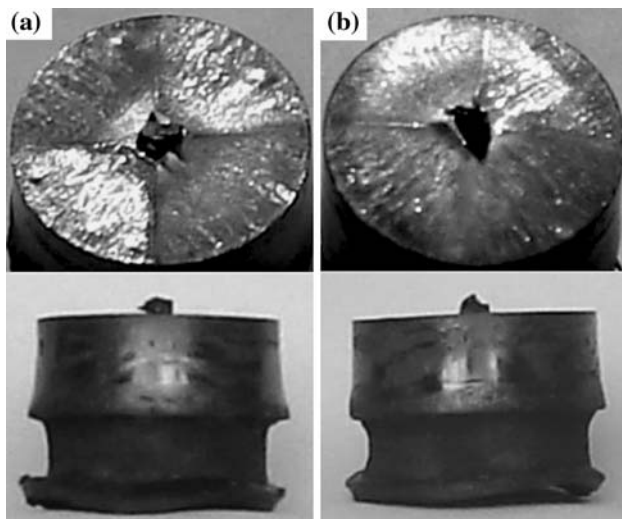


Fig. 2 Top and side view of the GdBCO bulk superconductors grown with **a** RLS and **b** NLS by the TSIG technique in air

random nucleation probability of GdBCO grains, thus the crystal growth from the seed can expand over the whole upper surface easily and steadily for each sample as long as the liquid was sufficient. Furthermore, from the side view, no slope or collapse of the whole arrangement and heavy deformation of the upper grown GdBCO crystal were observed for the samples after heat treatment process, which proved the feasibility of the two liquid sources for the TSIG process.

Figure 3 shows the scanning electron micrographs (SEM) of the GdBCO samples, and each micrograph was scanned at the outmost position of top surface for each sample, i.e., just at the edge of the top surface. For both the two samples, firstly, no pores with a size over $10\ \mu\text{m}$ were observed. Secondly, the size distribution of granular Gd-211 particles is in the range from submicron to $10\ \mu\text{m}$, and serious segregation or cluster of Gd-211 particles was not observed, which all indicated the superiority of the TSIG technique. Furthermore, the average size and volume fraction of Gd-211 second phase particles in Gd-123 matrix were analyzed qualitatively using the image processing software (ImageJ) (<http://rsbweb.nih.gov/ij/>). The results indicated that, the volume fraction of Gd-211 particles, V_{f211} , was about 35% for the two samples. Such a high V_{f211} value was obtained here maybe because that the micrographs were scanned from *a* growth sector and at a position so far away from the seed [6, 14, 15]. The average size values of Gd-211 particles for the two samples, analyzed by assuming that the shape of the Gd-211 particles is spherical, are estimated as 2.39 and $2.28\ \mu\text{m}$, respectively, which have no evident difference. This result may be anticipated by the following that the samples were fabricated with the same batch of Gd-211 precursor powder and

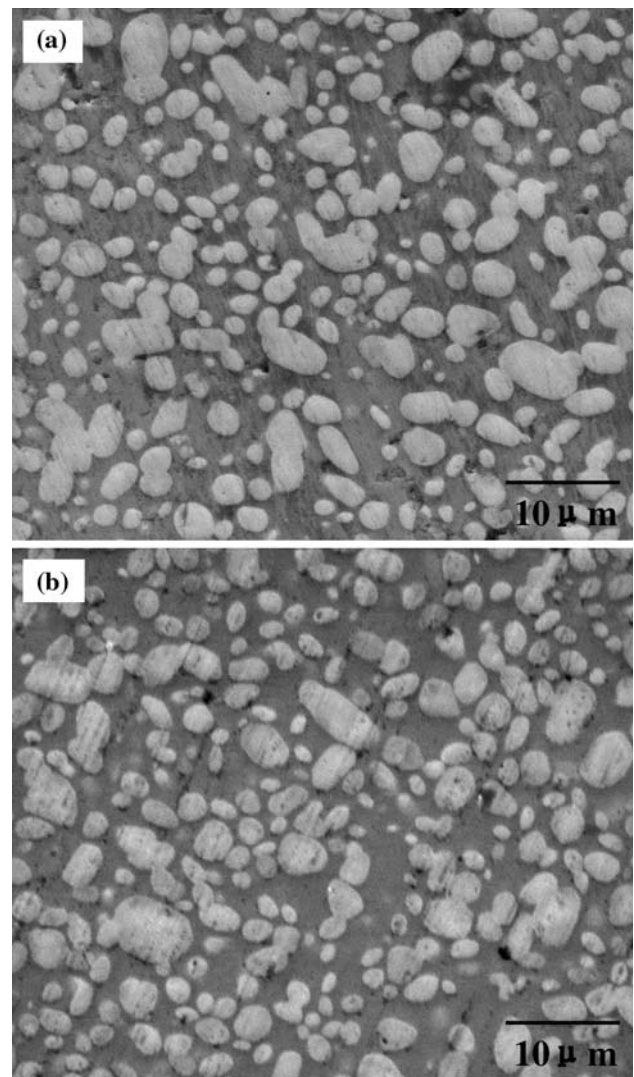


Fig. 3 SEM micrographs of the GdBCO samples grown with **a** RLS and **b** NLS

through the same heat treatment process. But, these values are rather greater than the results obtained for Pt-added GdBCO single grains melt processed in air by Shi et al., whose results are mainly in a range from 0.90 to $1.30\ \mu\text{m}$ [16]. As a result, it can be concluded that, addition of impurity phases (such as Pt or CeO_2 , etc.) to the precursor powder is an effective way to suppress Gd-211 ripening in the molten Ba–Cu–O liquid, and this processing is really essential for improvement of the superconducting properties, even in the IG process.

The levitation forces of the samples were measured under a zero-field cooling state at 77 K by a self-made device [17, 18]. A magnet ($\varnothing\ 30\ \text{mm}$) with a surface field of 0.5 T was used in the levitation force measurements. The maximum levitation force measured in this experiment was achieved at the smallest gap (0.1 mm) between the two nearest surfaces of the sample and the magnet. The

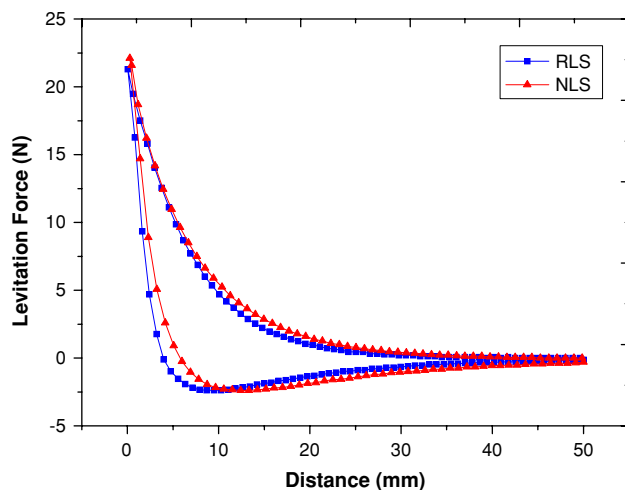


Fig. 4 The levitation forces versus distance at 77 K for the single-domain GdBCO bulk samples

levitation force values versus distance with the magnet for the samples are shown in Fig. 4. As we can see from the figure, the maximum levitation forces for the two samples are 21.3 and 22.1 N, respectively, which have not much difference. This result indicates that, based on the NLS, GdBCO single grains fabricated by the TSIG technique have the same superior and reliable performance just as the RLS, which proves the usability of the NLS for the TSIG technique in practice. The maximum levitation forces for the two samples, however, are in the range of 6–7 N/cm², which are lower than the results by other laboratories for GdBCO. This observation can be considered as a result of the larger Gd-211 particles in the microstructure of the samples as shown in Fig. 3.

The small ascendance in levitation force of the sample by NLS may be attributed to the superiority of this liquid source. The Gd-200 phase applied in NLS is the commercially available powder of 99.99% purity, which contains hardly any carbon. But the Gd-123 phase in RLS is prepared from a composition with large amount of BaCO₃. The residual carbon in Gd-123 will transfer into the upper sample with the liquid at high temperature, leading to a decline of superconducting properties in the final bulk. As a result, employment of the NLS for the TSIG process can bring positive effects on the improvement of bulk properties.

Conclusions

Single-grain GdBCO bulk superconductors have been fabricated in air using the RLS and NLS by the TSIG

technique, respectively. After detailed investigations in morphology, microstructure, and levitation force of the grown samples, it can be concluded that, the two necessary conditions for one powder used as liquid source: (i) support the Gd-211 preform and keep the whole sample upright during the heat treatment process; (ii) supply sufficient Ba–Cu–O liquid phase for growth of Gd-123 crystal, can be quite satisfied by the new composition proposed in this article. After employing this NLS, the TSIG process is much simplified, because only two precursor powders are needed to prepare for the whole process flow.

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References

- Cardwell DA (1998) Mater Sci Eng B 53:1
- Li F, Vipulanandan C, Zhou YX, Salama K (2006) Sup Sci Technol 19:589
- Chen YL, Chan HM, Harmer MP, Todt VR, Sengupta S, Shi D (1994) Physica C 234:232
- Reddy ES, Rajasekharan T (1998) Sup Sci Technol 11:523
- Meslin S, Noudem JG (2004) Sup Sci Technol 17:1324
- Iida K, Babu NH, Shi Y, Cardwell DA (2006) Sup Sci Technol 19:S478
- Babu NH, Iida K, Shi Y, Cardwell DA (2005) Appl Phys Lett 87:202506
- Meslin S, Harnois C, Chateigner D, Ouladdiaf B, Chaud X, Noudem JG (2005) J Eur Ceram Soc 25:2943
- Meslin S, Iida K, Babu NH, Cardwell DA, Noudem JG (2006) Sup Sci Technol 19:711
- Noudem JG, Meslin S, Horvath D, Harnois C, Chateigner D, Eve S, Gomina M, Chaud X, Murakami M (2007) Physica C 463–465:301
- Fang H, Ravi-Chandar K (2000) Physica C 340:261
- Fang H, Zhou YX, Ravi-Chandar K, Salama K (2004) Sup Sci Technol 17:269
- Yang WM, Zhou L, Feng Y, Zhang PX, Zhang CP (2006) J Alloy Comp 415:276
- Endo A, Chauhan HS, Shiohara Y (1996) Physica C 273:107
- Shi Y, Babu NH, Iida K, Cardwell DA (2007) IEEE Trans Appl Supercond 17:2984
- Shi Y, Babu NH, Iida K, Cardwell DA (2007) Sup Sci Technol 20:38
- Yang WM, Zhou L, Feng Y, Zhang PX, Wu MZ, Wu XZ, Gawalek W (1999) Rare Metal Mater Eng 28:231
- Yang WM, Chao XX, Shu ZB, Zhu SH, Wu XL, Bian XB, Liu P (2006) Physica C 445–448:347