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Processing conditions for (Nd, Eu, Gd)-Ba-Cu-O ternary bulk superconductors

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Abstract

(Nd, Eu, Gd)-Ba-Cu-O ternary bulk superconductors have high potential for practical applications since they exhibit very high critical current densities and thus high field trapping capabilities. (Nd, Eu, Gd)-Ba-Cu-O superconductors are synthesized in a reduced oxygen atmosphere, which requires a control of oxygen partial pressure and needs a special device for hot seeding. In the present study, for simplicity, we employed Ar gas flow into the furnace to control oxygen partial pressure instead of flowing oxygen-controlled gas. Hence, it was necessary to modify the melt processing conditions to produce a single domain. Through the optimization of seeding temperature and cooling rate, we obtained the processing conditions, in which a single domain bulk (Nd, Eu, Gd)-Ba-Cu-O of 20 mm diameter could be synthesized.

Keywords: Ternary bulk superconductors; (NEG)-Ba-Cu-O; Melt processing

1. Introduction

(Nd, Eu, Gd)-Ba-Cu-O (NEG) superconductors exhibit critical current density (J_c) of about 60,000-100,000 A/cm^2 at 3 T, 77 K [1-4] which is higher than those of Y-Ba-Cu-O by almost one order of magnitude. Such high J_c values of this system have high advantage over other RE-Ba-Cu-O (RE: rare earth elements) for practical applications for which one needs strong magnetic fields and field gradients like a superconducting magnetic separation system and a drug delivery system. The NEG system also exhibits extremely high irreversible field exceeding 7 T at 77 K [2], which is attractive for high field applications at this temperature. Such a high field application is difficult for most high T_c superconductors at 77 K due to a low irreversibility field caused by thermal agitation [5]. However, good quality NEG materials are grown with the oxygen-controlled melt-growth (OCMG) process, for which oxygen partial pressure in the environment must be carefully controlled on the level of 0.01-0.1 %. In addition, the batch processing conditions for producing multiple NEG superconductors have not yet been established. The batch process will lead to the mass production and therefore the cost reduction to enhance the competitiveness of NEG superconductors in the engineering market. In this study, we fabricated several NEG bulk samples with homemade powders of (Nd, Eu, Gd)$Ba_2Cu_3O_y$ (NEG123) mixed with (Nd, Eu, Gd)$BaCuO_5$ (NEG211) and Gd_2BaCuO_5 (Gd211) in a molar ratio of 5:1. Here we selected Gd211 as a second phase in addition to NEG211, since it has been reported that Gd211 addition is effective in reducing the particle size and thereby enhancing the critical current density [6]. Instead of flowing oxygen-reduced gas, we melt processed the samples by simply flowing Ar gas into the box-type electric furnace, under open atmosphere. The benefit of the present process is that the seed crystal can be placed on the sample surface like conventional hot seeing process. However, the melt processing conditions have to be modified again to fabricate a single domain bulk superconductor.

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2. Experimental

We synthesized the ternary NEG-123 and NEG-211 powders from commercial Nd_2O_3, Eu_2O_3, Gd_2O_3, BaO_2 and CuO powders. These initial powders were weighed to form $(Nd_{0.33}Eu_{0.33}Gd_{0.33})$ $Ba_2Cu_3O_y$ and $(Nd_{0.66}$ $Eu_{0.66}$ $Gd_{0.66})$ $BaCuO_5$. They were mixed in a mortar and pestle for two hours. The well mixed powders were calcined at 880°C for 24 hours. The calcined powders were thoroughly ground to fine powder again and repeated for another two cycles. We then mixed NEG-123 and NEG-211 powders in a molar ratio of 5:1. Likewise, commercial Gd-211 powders and NEG123 mixed in a molar ratio of 5:1. These mixed powders were pressed into pellets 20 mm in diameter and 10 mm in thickness under the pressure of about 100 MPa. For melt-processing, we used the Nd123 and 2wt% MgO doped as a seed crystal. MgO-doped Nd123 has a higher decomposition temperature than Nd123 [7], which is effective in avoiding the decomposition or the reaction of the seed during the top-seeded melt-growth process.

Figure 1 shows the thermal profile for melt-processing, in which we need to control two parameters: seeding temperature (Ts) and cooling rate (Y). Here we employed hot seeding technique throughout the whole study because the maximum temperature in the thermal program was about 1125°C which was higher than the decomposition temperatures of the Nd123 and MgO-doped Nd123 seed, and hence cold-seeding technique is not applicable. During the melt-process, we introduced Ar gas into the furnace through a small pipe connected to Ar source without any shielding. Thus Ar gas was kept to flow in and out of the furnace until the completion of grain growth at 990°C. This will enable us to maintain reduce-oxygen atmosphere during the melt-growth process. This method is simple and thus suitable for mass production.

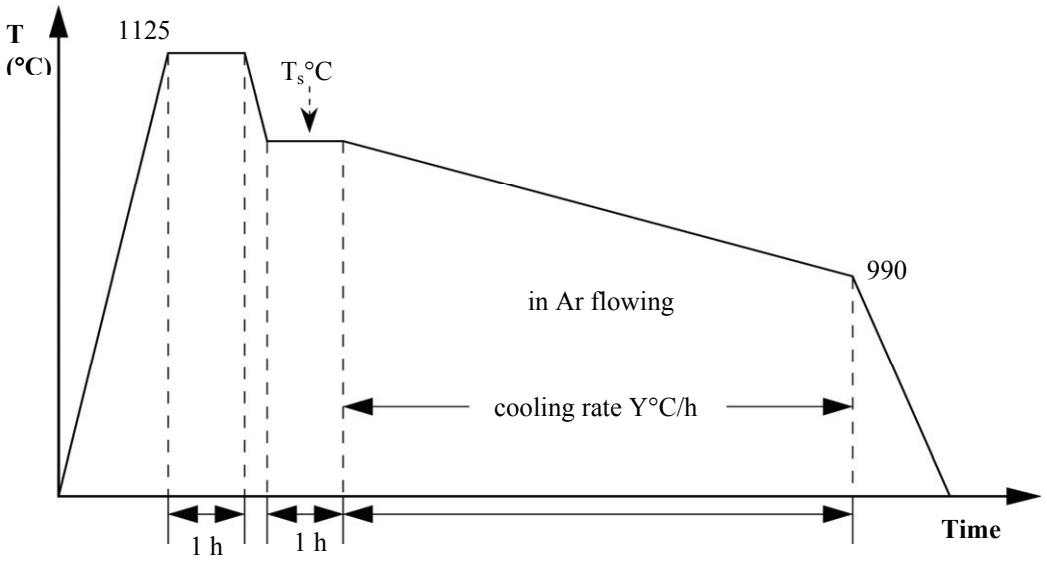

Fig. 1. Thermal profile for melt processing, for which we need to control two parameters: seeding temperature (T_s) and cooling rate (Y).

In order to determine the processing conditions, we first measured the decomposition temperatures of NEG samples. Table 1 shows the decomposition temperatures of NEG123+NEG211 and NEG123+Gd211 when they were well mixed in a molar ratio of 5:1 measured with differential thermal analyses (TG-DTA, Brukers Inc.).

Table 1. The decomposition temperatures of NEG123 + NEG211 and NEG123 + Gd211

sample	molar ratio	decomposition temperature (°C)
NEG123+NEG211	5:1	1042.0
NEG123+Gd211	5:1	1045.7

The decomposition temperatures of NEG123+NEG211 and NEG123+Gd211 samples were 1042.0 and 1045.7°C, respectively. Based on these results, we optimized processing conditions.

3. Results and discussion

For the first batch, we selected 1040°C as a seeding temperature based on the results of TD-DTA measurements presented in Table 1. We used a Nd123 seed crystal that is commonly used for melt-processing of Y-Ba-Cu-O samples. For hot-seeding, we opened the furnace door at this temperature and placed the Nd123 seed such that its (001) surface sit on the sample surface. This kind of hot seeding technique has been established in our laboratory and can be performed without any difficulty. After hot seeding, the samples were slowly cooled at a rate of 0.4°C/hr for grain growth.

Figure 2 shows the photos of NEG123+NEG211 and NEG123+Gd211 bulk samples after the melt growth. One can see that NEG123 grains were nucleated from the seed, however, the grain growth was not extended to the sample edge due to spontaneous nucleation. Such a multiple nucleation is ascribed to a fast cooling rate. We then lowered a cooling rate down to 0.3°C/hr, however, single grain growth was not achieved.

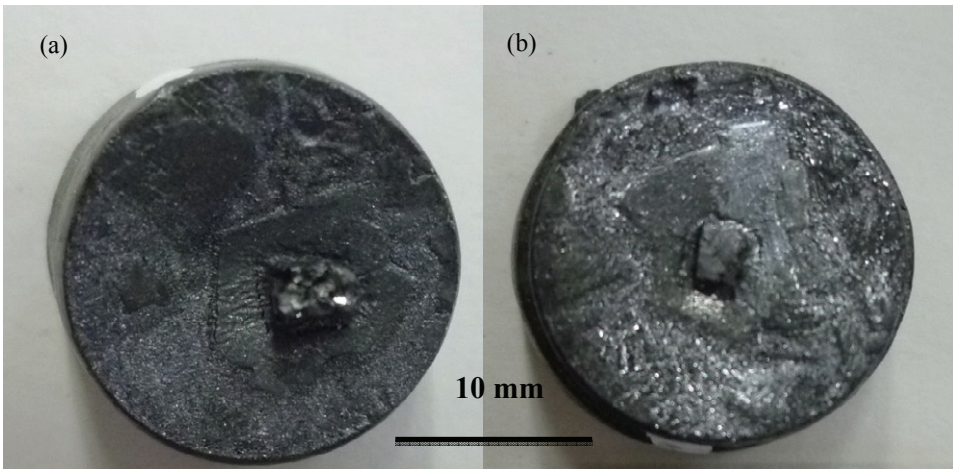

Fig. 2. Photos of (a) a NEG-123 mixed with 20 mol% NEG-211 sample and (b) a NEG-123 mixed with 20 mol% Gd-211 sample when they were grown at a cooling rate of 0.4°C/h with a seeding temperature of 1040°C.

For achieving single grain growth, a seeding temperature is also important. In particular, during the hot seeding process, the furnace temperature is slightly lowered, since we must open the furnace door. We then increased the seeding temperature from 1040 to 1060°C. However, we found that Nd123 seed reacted with the samples at this high temperature. Hence, we employed Nd123 doped with 2wt%MgO as a new seed crystal, since the melting point of the seed can be increased by MgO doping [7].

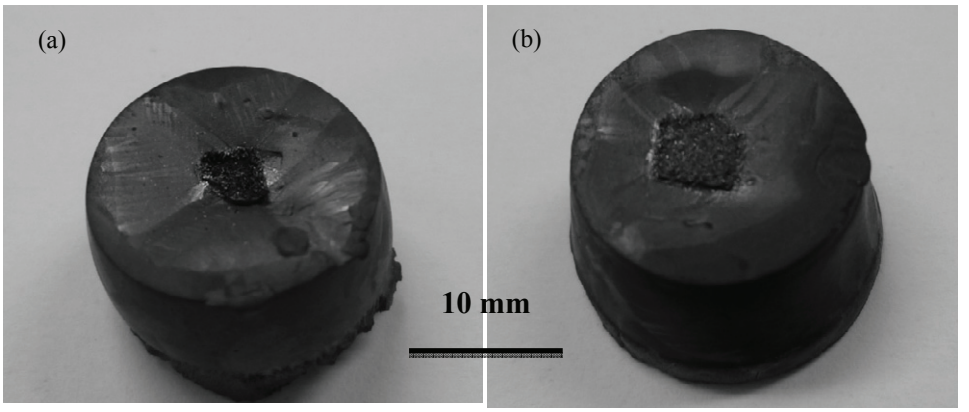

Fig. 3. Photos of (a) NEG-123 with 20 mol% NEG-211 sample, and (b) NEG-123 with 20 mol% Gd-211 samples when the samples were grown at a cooling rate of 0.3°C/h ith a seeding temperature of 1060°C.

Figure 3 shows photos of NEG123+ NEG211 and NEG123+Gd211 samples seeded at 1060°C using MgO-doped Nd123 crystal followed by slow cooling at a rate of 0.3°C/h. The surface morphologies of these samples showed that grains were nucleated from the seed and extended to the sample edge.

The present results suggest that the single grain growth of NEG samples is possible with top-seeded melt-growth process based on hot-seeding technique when melt-processing conditions are optimized even under Ar gas flowing condition.

4. Summary

We have succeeded in fabricating single domain sample of ternary bulk NEG-123 mixed with either NEG-211 or Gd211 in a molar ratio of 5:1 of 20 mm diameter in Ar gas flowing atmosphere. The samples were all synthesized using a simple box furnace without any help of complicated skill for hot seeding process. The melt processing conditions were studied and modified to obtain optimal conditions for our study, in which single domain samples could be grown at the seeding temperature of 1060 °C and slow cooling at 0.3 °C/h until 990°C using Nd-123 seed crystal doped with 2wt% MgO in flowing Ar gas. These developed conditions might be applicable to a massive batch production to reduce the cost and complexity of synthesizing NEG ternary bulk superconductors in the further study.

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