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Fabrication of high performance Gd–Ba–Cu–O single grains in air using a practical melt processing technique

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ABSTRACT

A practical processing route for the fabrication of LRE-Ba–Cu–O single grain superconductors has been developed at the University of Cambridge based on a generic, Mg-doped Nd-123 melt textured seed and suppression of the formation of the solid solution phase in air by enriching the precursors with higher Ba concentration. The processing of high performance Gd–Ba–Cu–O single grains using this processing route is described. The Mg-doped generic seed crystal has been used effectively to promote heterogeneous nucleation via a cold-seeding process. The Gd/Ba solid solution has been suppressed by enriching Gd–Ba–Cu–O precursor powders with two different Ba-rich compositions. This involved adding BaO_2 and $GdBa_6Cu_3O_y$ (Gd-163) (a novel Ba-rich second phase) to the precursor powders, respectively. The Gd-163 phase has been observed not only to suppress formation of the solid solution phase, but also to promote increased heterogeneous grain size. A detailed further study has been carried out with an initial aim of optimizing the BaO_2 and Gd-163 phase content of the precursor composition to produce a single grain almost free of solid solution. Based on the optimized parameters, large single grain Gd–Ba–Cu–O superconductors have been fabricated in an air atmosphere and demonstrated to exhibit record trapped magnetic fields for this material melt processed in air in relatively small single grain samples. The trapped fields of samples produced in air atmosphere are at least comparable to those processed under reduced oxygen partial pressure.

1. Introduction

(LRE)–Ba–Cu–O (where LRE = a Light Rare Earth element such as Nd, Sm, Eu and Gd) bulk superconductors, exhibit high T_c and J_c compared to (RE)–Ba–Cu–O (where RE = Y, Yb, Tm, Er, Ho and Dy) materials when processed under reduced oxygen partial pressure [1]. The critical current density, J_c, and irreversibility fields of (LRE)–Ba–Cu–O superconductors at 77 K, for example, are generally significantly higher than the corresponding values observed for Y–Ba–Cu–O (YBCO) [2–5]. However, high performance (LRE)–Ba–Cu–O single grain superconductors are fabricated typically by a hot-seeding technique under a controlled, reduced oxygen partial pressure (PO_2) atmosphere. As a result, specially designed furnaces are required in which a seed crystal of the same composition as the bulk (LRE)–Ba–Cu–O precursor pellet is used typically to seed the peritectically decomposed sample without disturbing the processing atmosphere. The requirement for controlled, reduced oxygen partial pressures and the lack of a suitable seed crystal, therefore, represent real barriers to the development of a practical fabrication process for (LRE)–Ba–Cu–O bulk superconductors. As a result, the successful fabrication of single grain (LRE)–Ba–Cu–O bulk materials has been limited to a few, mainly academic, research groups [6–8]. This is in contrast to the processing of YBCO, which can be fabricated under air using readily-available seed crystals with the required structural and chemical properties [9–12]. The lack of a practical processing method for (LRE)BCO single grains, on the other hand, has hindered severely their development to date for engineering applications.

Recently a practical processing method for the fabrication of (LRE)BCO single grains has been developed at the University of Cambridge [13]. The process is based initially on the development of a new type of generic seed crystal that can promote effectively the epitaxial nucleation of any (RE)–BaCuO system [14] and, secondly, on the suppression of the formation of (LRE)/Ba solid solution in a controlled manner within large LRE–Ba–Cu–O grains melt processed in air.

The Gd–Ba–Cu–O (GdBCO) system has been selected from the various (LRE)–Ba–Cu–O systems as the focus of the present study because the average size of Gd_2BaCuO_5 (Gd-211) inclusions in the microstructure of melt processed GdBCO single grains is known to be smaller than that of other (RE)–Ba–Cu–O bulk superconductors

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[15]. In addition, it has been demonstrated that this system can trap record trapped magnetic fields of up to 3 T at 77 K for a single grain of diameter 65 mm [16]. Several attempts to grow GdBCO large, single grins have been reported in the literature [17–19] mainly via the hot-seeding technique. Extensive research has been carried out at Cambridge over the past three years to develop a practical processing route for the Gd–Ba–Cu–O system [20]. This paper describes the important characteristics of the new generic seed and the suppression of the formation of Gd/Ba solid solution by enriching the Gd–Ba–Cu–O precursors with two different Ba-rich precursor compositions [20]. This involved adding BaO_2 and $GdBa_6Cu_3O_y$ (Gd-163), a novel Ba-rich second phase, to the precursor powders, respectively. Finally, a detailed study has been carried out to optimize BaO_2 and Gd-163 phase content in fully processed bulk superconductors to obtain a nearly solid solution free single grain. The fabrication of large, single grain Gd–Ba–Cu–O superconductors in air with record trapped magnetic fields is reported based on these optimized parameters.

2. Experimental

2.1. Generic seed crystal

Mg-doped generic seed crystals were fabricated by conventional melt processing [14]. Initially, precursor powders with starting compositions of Nd-123 + 12 mol% Nd-422 + 1 wt% MgO were pressed uniaxially into pellets and melt processed under air with the temperature profile shown in Fig. 1a. In this process, T_m, T_{g1}, T_{g2} and R were 1140 °C, 1110 °C, 1050 °C and 0.5 °C/h, respectively. The resultant melt processed pellet typically contained randomly oriented multi-grains, which could be cleaved easily along their crystallographic *ab*-planes to produce a large number of small, single grains [14].

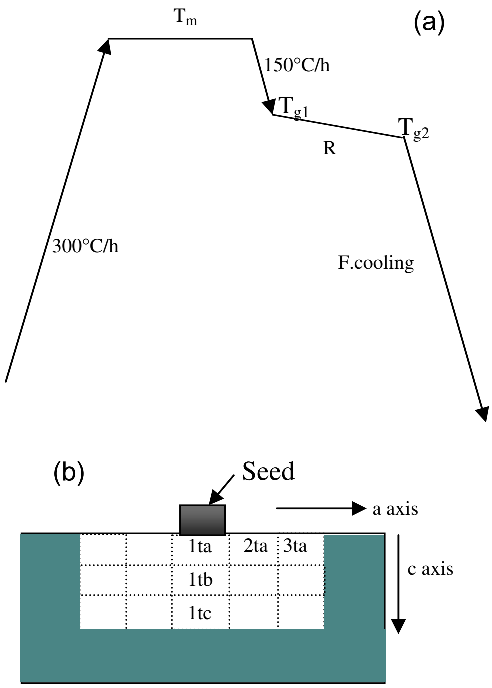

Fig. 1. (a) The temperature profile used for melt-processing the various precursor pellets in air. (b) Schematic illustration of the cross-section of a single grain and the position of specimens along the *a* and *c*-axes cut for magnetic J_c measurements using a SQUID magnetometer.

2.2. Precursor synthesis

$GdBa_2Cu_3O_{7-\delta}$ (Gd-123), Gd_2BaCuO_5 (RE-211) and $GdBa_6Cu_3O_y$ (Gd-163) single phase powders were synthesised via a conventional solid state reaction process from Gd_2O_3, BaO_2 and CuO starting materials. All mixed powders were calcined in air with several intermediate grinding stages until X-ray diffraction (XRD) confirmed the presence of a single phase. The XRD pattern for single phase Gd-163 is reported elsewhere [21].

2.3. Fabrication of Gd–Ba–Cu–O single grains in air with excessive BaO_2

Excess BaO_2 was added to the precursor composition in order to suppress Gd/Ba solid solution formation during melt processing [22]. Precursor powders of Gd-123 + 30 wt% Gd-211 + Z wt% BaO_2 + 0.1 wt% Pt, where Z = 0, 1, 2, 4 and 10, were mixed thoroughly using a mortar and pestle and pressed uniaxially into cylindrical pellets. A small ($1.5 \times 1.5 \times 1\ mm^3$) Mg-doped NdBCO melt processed grain was placed, prior to melt processing (i.e. by the so-called cold seeding technique), on the top of each pellet with the *ab*-plane of the seed in direct contact with the surface of the sample. Samples were initially heated rapidly in air in a box furnace to the melting temperature, T_m, held for 0.6 h to ensure complete peritectic decomposition of the Gd-123 phase, cooled rapidly to T_{g1} and held for various time intervals varying from 4 to 40 h, corresponding to varying degrees of undercooling [20] prior to furnace cooling.

2.4. Fabrication of Gd–Ba–Cu–O single grains in air with excess novel Gd-163 phase

The precursors powders with starting compositions of 70 wt% Gd-123 + (30 − X) wt% Gd-211 + X wt% Gd-163 + 0.1 wt% Pt, where X = 5, 10, 15, and 30, were mixed thoroughly and pressed uniaxially into pellets and melt processed using a small, generic seed crystal. The thermal profile used in this study is also described in Fig. 1a, where T_{g1} is the growth temperature in the range of 1040–1035 °C depending on the peritectic decomposition temperature, T_p, of the different precursors, which were measured by differential thermal analysis (DTA).

2.5. Fabrication of high performance Gd–Ba–Cu–O single grain in air

Ag was added to the precursor powder to suppress the formation of cracks oriented within the *ab* and *ac* crystallographic planes of the samples during the melt growth and oxygenation processes. Precursors with composition 75 wt% Gd-123 + 25 wt% Gd-211 + 1 wt% BaO_2 + 10 wt% Ag_2O + 0.1 wt% Pt were pressed uniaxially into pellets of diameter 32 mm and, again, melt processed using a Mg-doped Nd–Ba–Cu–O generic seed. The single grain was grown in a box furnace with the temperature profile shown in Fig. 1a for T_m = 1050, T_{g1} = 1018 and T_{g2} = 980 with R = 0.3 °C/h.

Small samples were cut from the melt processed parent bulk, as illustrated schematically in Fig 1b for measuring the spatial variation of T_c within the bulk microstructure. Superconducting properties such as T_c, J_c (for the small samples) and trapped field (for the large, as-processed bulk) were measured after annealing in oxygen in the temperature range 440–360 °C in a flowing O_2 atmosphere between 100 and 300 h, depending on sample size.

3. Results and discussion

The required properties of a generic seed crystal suitable for melt processing (LRE)–Ba–Cu–O bulk superconductors, such as