Growth Rate and Superconducting Properties of Gd-Ba-Cu-O Bulk Superconductors Melt Processed in Air

Y. Shi, N. Hari Babu, K. Iida, and D. A. Cardwell

***Abstract*—A generic Mg-doped Nd-Ba-Cu-O seed crystal has been developed recently for the fabrication of any type of rare earth (RE) based (RE)-Ba-Cu-O single grain bulk superconductor in air. The new generic seed simplifies significantly the top seeded melt growth (TSMG) process for light rare earth based (Nd, Sm, Gd, or mixed rare earth elements) bulk superconductors, in particular. GdBCO single grains have been fabricated successfully in air using the new seed in a cold-seeding process. In this study, precursor powders were enriched with different amounts of BaO_2 to investigate the extent of substitution of Gd for Ba in the $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ solid solution phase. The growth process of large single grains in air was investigated at various growth temperatures under isothermal processing conditions. Crystal growth rate as a function of under-cooling and BaO_2 content has been determined from these experiments. The spatial variation of T_c and transition temperature width for applied field aligned along the a/b and c-axis of grains fabricated with different BaO_2 content has also been investigated in order to understand the extent of the formation of Gd/Ba solid solution with varying growth temperature and precursor composition. These results have been used to establish the optimum conditions for fabricating solid solution-free, large single grains of GdBCO in air.**

***Index Terms*—GdBCO, growth rate, microstructure, superconducting properties.**

I. Introduction

MELT processed (LRE)-Ba-Cu-O superconductors [(LRE)BCO], where LRE is a light rare earth element such as Nd, Sm, Eu and Gd, are known to exhibit higher critical current densities, J_c's, and higher irreversibility fields than Y-Ba-Cu-O (YBCO) [1]–[3]. However, it has not been possible to date to fabricate (LRE)BCO single grains in air using a practical growth technique, such as top seeding melt growth (TSMG), due primarily to the absence of a suitable seed crystal. A recently developed MgO-doped NdBCO seed crystal [4], [5] has enabled the fabrication of (LRE)BCO superconductors in the form of single grains in air by the TSMG process for the first time.

The Gd-Ba-Cu-O (GdBCO) system has been chosen in the present study because the average size of Gd_2BaCuO_5 (Gd-211) second phase inclusions in the microstructure of melt processed single grains is known to be smaller than that is the average size of inclusions in any other (RE)-Ba-Cu-O compound. 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 [6]. Several attempts to grow large, single grains of GdBCO have been reported using hot-seeding techniques [7]–[10]. As with other (LRE)BCO systems, the transition temperature of GdBCO decreases with increasing solid solution formation (i.e. with increasing x in $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$. Unlike the NdBCO and SmBCO systems, however, the transition temperature of GdBCO bulk superconductors does not appear to decrease significantly when these materials are fabricated in air by a hot seeding technique [8]. In addition, solid solution phase formation can be suppressed by enriching the precursor powder with either $BaCuO_{2-\delta}$ or BaO_2 [9], [10]. Although large single grains of GdBCO have been fabricated in reduced oxygen partial pressure by a hot-seeding technique, the growth process itself is relatively un-researched. It is necessary, therefore, to study further the growth of GdBCO single grains in air so that larger single grains with better properties can be fabricated using the TSMG process.

In this paper, we investigate the growth rate of large GdBCO single grains fabricated by TSMG in air under isothermal cooling conditions using a generic MgO-NdBCO seed. We report the microstructure and superconducting properties of the samples fabricated by this process.

II. Experimental

Gd_2BaCuO_5 (Gd-211) powder was prepared by mixing commercially available Gd_2O_3, CuO and $BaCO_3$ powders of 99.9% purity followed by repeated calcinations at 900°C for 12 hours until X-ray diffraction (XRD) confirmed the presence of a Gd-211 single phase. The fully calcined Gd-211 was then mixed with $Ba_3Cu_5O_8$ (99.9% Nexans Superconductors GmbH) in the following compositions; 70 wt% Gd-123 $(\text{Gd-211} + Ba_3Cu_5O_8)$ + 30 wt% Gd-211 + X wt% BaO_2 + 0.1 wt% Pt, where X = 0, 1, 2, and 4. Differential thermal analysis (DTA) in flowing air was carried out on the precursor powders prior to melt processing at temperatures up to 1150°C with a heating rate of 5 °C/min. The mixed powder was then pressed uniaxially into pellets of diameter 16 mm and thickness 5 mm under 5 MPa. An NdBCO seed crystal doped

Manuscript received August 29, 2006. This work was supported by EPSRC, UK.

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Digital Object Identifier 10.1109/TASC.2007.899474

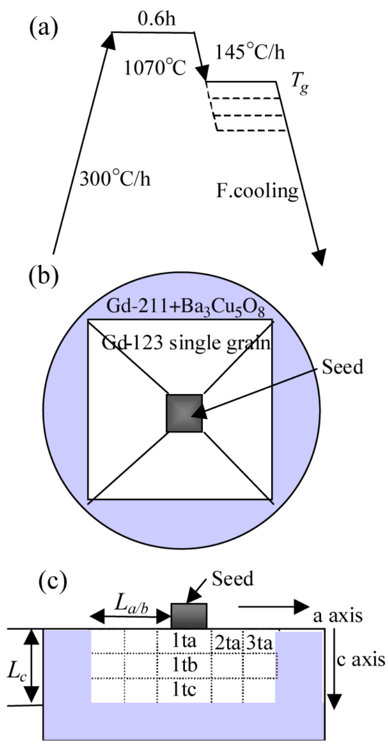

Fig. 1. (a) Temperature profile used to fabricate large single grains. (b) Top view of a single grain (square, white in contrast) solidified from the melt (shaded region) and (c) the cross section of the single grain.

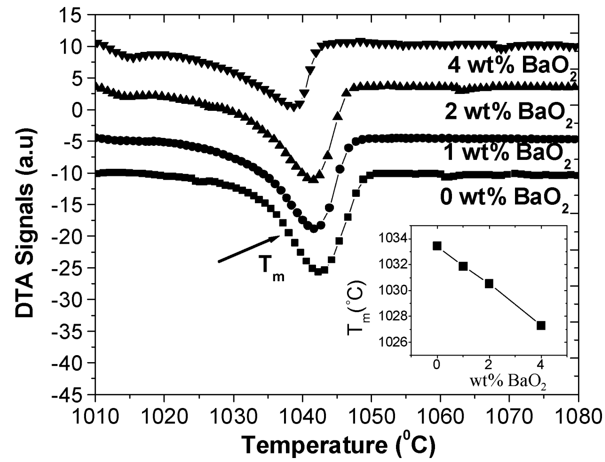

Fig. 2. DTA traces for precursor powder containing 70 wt% $\mathrm{Gd}-123+30$ wt% $\mathrm{Gd}-211+0.1$ wt% Pt + X wt% $\mathrm{BaO_2}$ for $\mathrm{X}=0$, 1, 2 and 4. The inset shows the measured Tm as a function of $\mathrm{BaO_2}$ content.

with 1 wt% MgO was placed on the top surface of each precursor pellet. The pellets were melt-processed isothermally (i.e. at a constant growth temperature, $\mathrm{T_g}$) in air by TSMG using the temperature profile shown in Fig. 1(a). The dashed lines in Fig. 1(a) represent different values of $\mathrm{T_g}$ $(1024 \sim 1035\ ^\circ\mathrm{C})$. $\mathrm{T_g}$ was chosen carefully to lie between the peritectic temperature, $\mathrm{T_p}$, and a temperature below which no recognizable, secondary inhomogeneous grain nucleation occurred from the melt. The growth time, t, was varied between 4 and 40 hours, following which the samples were cooled quickly to room temperature. A relatively high cooling rate of 1000 °C/h was used between $\mathrm{T_g}$ and 800 °C. As a result, any change in growth length of the solidified grain during the rapid cooling process was assumed to be negligible.

The large, single grains were heated to 440 °C in flowing oxygen and cooled to 360 °C at a cooling rate of 0.4 °C/h. Individual grains fabricated at various $\mathrm{T_g}$ were cut along the ac-plane [i.e. through the thickness of the grain; see Fig. 1(c)]. These specimens were polished and their microstructure investigated using a Nikon ECLIPSE ME600 optical microscope. NIH-image software [11] was used to analyze the average size and the area fraction of Gd-211 inclusions in the bulk microstructure. Fig. 1(b) and (c) illustrates the top view of a single grain and it's ac-plane cross section, respectively. The growth rate along the ab-plane is defined as $L_{a/b}/t$ [Fig. 1(c)], where $L_{a/b}$ is the length of single grain along the a/b axis and t is the growth time. Single grains with different compositions, processed at different temperatures, were cut into small pieces to investigate the spatial variation of $\mathrm{T_c}$ across the grain. The dashed lines in Fig. 1(c) illustrate how each grain was sub-sectioned. $\mathrm{T_c}$ of the resulting specimens was measured using a MPMS XL SQUID.

III. Results and Discussion

A. *Melting Point*

DTA was performed on precursor powders of 70 wt% Gd-123 + 30 wt% Gd-211 + 0.1 wt% Pt containing various amounts of $\mathrm{BaO_2}$ in order to investigate the influence of excess $\mathrm{BaO_2}$ on the peritectic temperature of the GdBCO system. The DTA traces are shown in Fig. 2. A so-called "two points" method, which is a built-in feature of the DTA apparatus, was used to determine the melting point of the precursor powder, $\mathrm{T_m}$, in each case. It can be seen from the inset to Fig. 2 that the melting point of the precursor powder decreases by about 5 °C as the $\mathrm{BaO_2}$ composition increases from 0 to 4 wt%. The measured melting point from DTA may be taken reasonably to represent the peritectic temperature, $\mathrm{T_p}$, of the powder, providing a very slow heating rate is employed in the measurement. As a result, Fig. 2 suggests that $\mathrm{T_p}$ of the precursor powder decreases with increasing $\mathrm{BaO_2}$ content.

B. *Influence of Change in Composition and T_g on T_c of Single Grains*

Fig. 3(a)–(d) shows the spatial variation of $\mathrm{T_c}$ along the a/b-axis of single grains grown from precursor powders prepared with different $\mathrm{BaO_2}$ content. $\mathrm{T_c}$ is observed to increase progressively from 89.3 K to 92 K as the crystal growth proceeds for the sample fabricated without $\mathrm{BaO_2}$ [Fig. 3(a)]. $\mathrm{T_c}$ of a small sample cut from under the seed position is the lowest and $\Delta\mathrm{T_c}$ is the highest. Such a variation in $\mathrm{T_c}$ as a function of position from the seed position is typical for LRE-BCO superconductors processed in air since the solid solution level in the vicinity of the seed is greatest. Also, the extent of the solid solution range decreases as the growth of the crystal proceeds [12]. Significantly, the measured value of $\mathrm{T_c}$ immediately under the seed increases when a small amount of $\mathrm{BaO_2}$ (typically 1 or 2 wt%) is added to the precursor, which

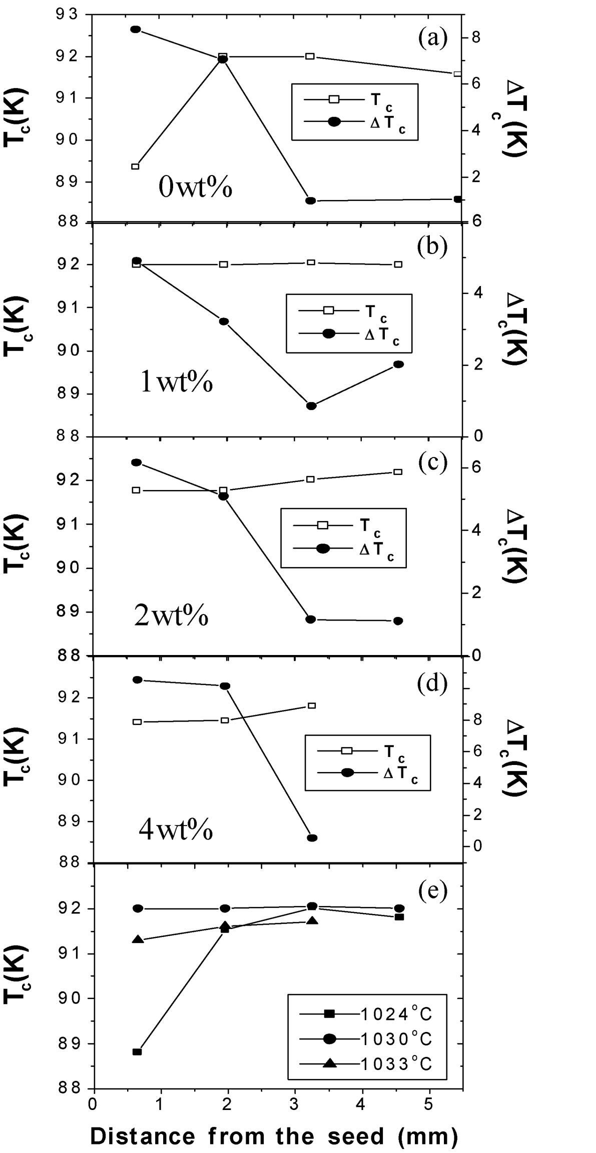

Fig. 3. Spatial variation (distance from the seed crystal position along the a/b-axis of the grain) of T_c and ΔT_c of single grains grown at 1030 °C for 12 hours from precursor powders with starting compositions of 70 wt% Gd-123 + 30 wt% Gd-211 + 0.1 wt% Pt enriched with (a) 0 wt% BaO_2 (b) 1 wt% BaO_2 (c) 2 wt% BaO_2 and (d) 4 wt% BaO_2. (e) Spatial variation of T_c for single grains grown at various growth temperatures from precursor powders enriched with 1 wt% BaO_2.

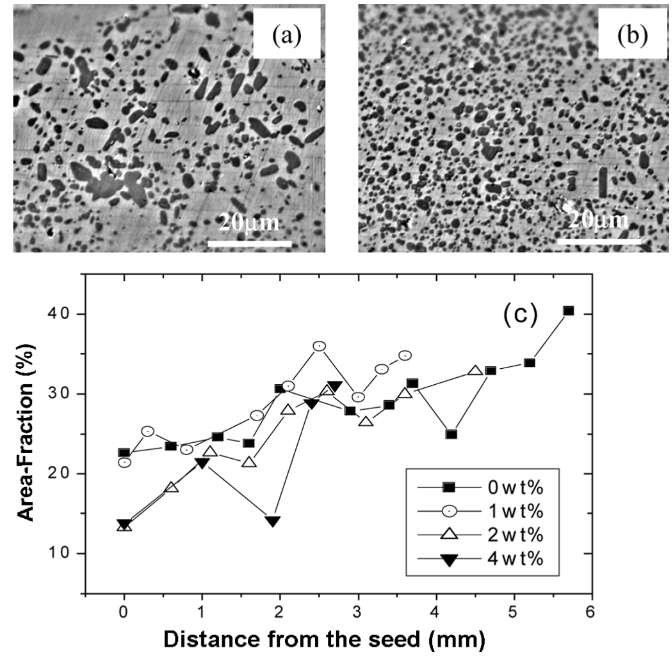

Fig. 4. Optical micrographs taken for specimens (a) under the seed (b) 2.1 mm away from the seed position in a/b direction for a single grain fabricated at 1030 °C from the precursor enriched with 1 wt% BaO_2 (c) Measured area fraction of Gd-211 as a function of distance from seed position along the a/b-axis of the single grain grown from precursors containing different amounts of BaO_2.

indicates a decrease in the level of solid solution formation. T_c for the sample containing 1 wt% excess BaO_2 is measured to be at least 92 K over the entire single grain along the a/b-axis, suggesting that the addition of a small amount of BaO_2 to the precursor powder suppresses Gd/Ba substitution (i.e. value of x in the formula $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ decreases with addition of 1–2 wt% BaO_2). T_c decreases slightly when up to 4 wt% BaO_2 is added to the precursor powder, but remains higher than 91 K over the entire grain. However, ΔT_c values are observed to increase [Fig. 3(d)] significantly in the samples containing 4 wt% BaO_2 in the vicinity of the seed crystal position.

Fig. 3(e) shows the spatial variation of T_c within a single grain processed from precursor powder enriched with 1 wt% BaO_2 at different temperatures. Grains grown under isothermal processing conditions at about 1030 °C have the highest T_c over entire singe grain, whereas grains fabricated either well above or well below this temperature exhibit relatively low T_c's.

C. Microstructural Features

Gd-211 inclusions in the Gd-123 matrix are observed generally to be inhomogeneous, as is the case for the YBCO system [13]. The average particle size in GdBCO is observed to decrease as a function of distance from the seed due to pushing of Gd-211 particles by the Gd-123 growth front. The average Gd-211 particles size is bigger [Fig. 4(a)] in the vicinity of the seed and smaller with distance from the seed position [Fig. 4(b)]. It is important to note that local microstructural inhomogeneities were observed in the vicinity of large voids and macro-cracks in the bulk sample, in particular. It should be mentioned that there is an error in determining the actual particle size and area distribution of the Gd-211 inclusions from the optical micrographs and the limitations of software HIM image used to analyze the particles. The area fraction of Gd-211 inclusions in the Gd-123 matrix [Fig. 4(c)] is observed to increase continuously as the distance from the seed increases. In particular, a low Gd-211 area fraction is observed in single grains containing 2 wt% and 4 wt% excess BaO_2 in the vicinity of the seed. The area fraction increases much more rapidly as the distance from the seed position increases in these samples.

D. Growth Rate

Single GdBCO grains were fabricated at various temperatures ranging from 1034 °C to 1024 °C. No grains of significant size were observed to nucleate from the seed for all starting compositions (i.e. containing 0, 1, 2 and 4 wt% BaO_2) when the

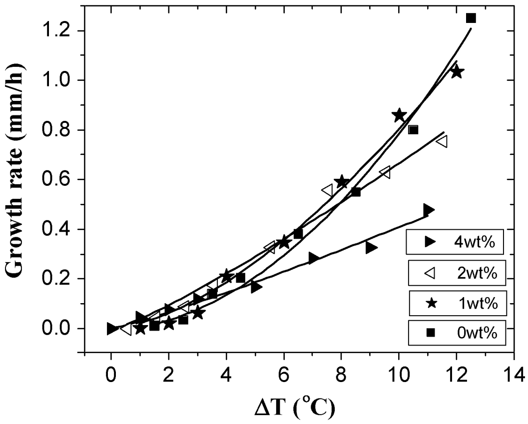

Fig. 5. Growth rate as a function of under-cooling for single grains containing different amounts of BaO_2.

TABLE I
GROWTH RATE FOR DIFFERENT BaO_2 CONTENTS

wt% of BaO_2	α	β
0	0.011	1.84
1	0.021	1.59
2	0.043	1.19
4	0.030	1.13

temperature of the melt was maintained at 1034 °C for 10–20 hours. However, grains of up to 1 mm in size were observed to nucleate and grow by increasing the growth time to 40 hours, suggesting that the peritectic temperature of these precursors is $>$ 1034 °C. Heterogeneous nucleation was not observed when the growth temperature was increased to 1037 °C, suggesting that T_p is just below this temperature. These results, combined with the DTA data shown in Fig. 2, enable T_p of the precursor compositions enriched with 0 wt%, 1 wt%, 2 wt% and 4 wt% BaO_2 to be estimated as 1036.5 °C, 1036 °C, 1035.5 °C and 1035 °C. The measured growth rate along the a/b-axis of the grain, $R_{a/b}$, as a function of under-cooling ΔT $(T_p - T_g)$ is shown in Fig. 5. The growth rate for all compositions increases with increasing under-cooling. The growth rate for the sample containing 4 wt% BaO_2 is very low even under the conditions of high under-cooling. This indicates that the growth of large, single grains from precursors enriched with 4 wt% BaO_2 is not practical. As in the case of YBCO [14] and NdBCO [15] systems, the relation between growth rate and under-cooling for GdBCO is observed to follow $R_{a/b} = \alpha(\Delta T)^{\beta}$ [where α and β are constants] for all compositions. Table I shows the fitted parameters. It can be seen that α and β vary systematically as the BaO_2 content changes from 0 wt% to 2 wt%; the sample with 4 wt% BaO_2 is an exception. The variation of α and β with composition suggests a different crystal growth mechanism for precursor compositions of different BaO_2 content. Further research is required to understand the observed variations in the growth kinetics of the GdBCO system.

IV. CONCLUSIONS

The growth process of GdBCO large single grains in air has been investigated for various growth temperatures under isothermal processing conditions. Crystal growth rate as a function of under-cooling and BaO_2 content has been investigated. The spatial variation of T_c and transition width along the a/b-axis of grains fabricated with different BaO_2 content shows that the addition of a small quantity of BaO_2 can suppress Gd/Ba substitution in the $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ solid solution phase. Based on these results, it is suggested that solid solution free, large GdBCO single grains can be grown in air using a precursor composition enriched with 1 wt% BaO_2 under isothermal condition for an under-cooling ΔT of ~ 5 °C.

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