Effect of growth temperature on properties of bulk GdBa$_2$Cu$_3$O$_y$ superconductors grown by IG process

Y. Nakanishi, S. Pavan Kumar Naik, M. Muralidhar* and M. Murakami

1Department of Materials Science and Engineering, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan

*miryala1@shibaura-it.ac.jp

Abstract. Recently, the flux pinning performance of Y-123 material was dramatically improved by optimizing the processing conditions during the Infiltration-Growth (IG) process. In the present work, we adapted the top-seeded IG technique and produced several 20 wt.% AgO$_2$ doped bulk GdBa$_2$Cu$_3$O$_y$ (GdBCO or Gd-123) samples at different growth temperatures of 983, 985, 986, 987, 989, and 992 °C with the same holding time of 25 h. Our results indicate that the bulk GdBCO samples dwelled at 986 °C is the optimum temperature to produce large Gd-123 growth without spontaneous nucleation. Magnetization measurements on 986 °C dwelled composite showed a sharp superconducting transition with \( T_c \), onset at 93.6 K. The critical current density at 77 K and self-field was 16,500 A/cm$^2$. The critical current density values are correlated with the microstructural changes in the bulk Gd-123 materials.

1. Introduction

Recently, the use of bulk LREBa$_2$Cu$_3$O$_{7-\delta}$ (LREBCO or LRE-123, with light rare-earth elements such as Y, Nd, Sm, Gd, etc.,) superconductors in various scientific and technological applications is increased due to their high trapping magnetic fields as compared to the conventional best permanent magnets available in the market [1, 2]. Producing single grained LREBa$_2$Cu$_3$O$_{7-\delta}$ (GdBCO or Gd-123) bulks is, therefore, important in various scientific and technological applications. Compared to YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO or Y-123), there is a chance to form a small fraction of solid solutions in GdBCO which contributes to the flux pinning. These solid solutions are of nanometre size and can effectively pin the flux at higher applied fields [4-7].

Over the past few decades, several groups have put efforts to introduce Ag into the LREBCO superconductors. In melt-growth (MG)-processed LREBCO superconductors a considerable work is done on the addition of Ag [8-10]. The introduction of Ag in LREBCO can modify the microstructures of the LREBCO superconductors; hence, the critical current density ($J_c$) and the mechanical properties are improved without reducing the $T_c$. A careful review of the literature clearly shows that the doped Ag fuses the gaps between the platelets and thus reduces the density of micro-cracks in the final composites. Furthermore, the non-superconducting 211 phase particles in the 123 matrix are refined [11-13] with the addition of Ag. In addition, the peritectic reaction temperature ($T_p$) at which the peritectic reaction of the LREBCO superconductors starts is lowered by $\sim 15$ °C to $30$ °C depending on the content of Ag added to the precursor [14-17]. Thus, the bulk LREBCO superconductors can be processed at very low temperatures and it is possible to control the 211 grain growth. Another important result of the Ag
addition is, due to the reduction in $T_p$, various 123 seeds with lower melting points can also be utilized for the fabrication of single grain bulks.

In our previous work [18] on the melt processed single grained mixed LREBCO sample, a systematic study of addition of Ag (5 wt.% to 30 wt.%) was investigated. The addition of 20 wt. % Ag$_2$O resulted in a large critical current density of 10 kA cm$^{-2}$, which was maintained even up to a field of 7 T at 77 K. Compared to the melt-growth process, the IG process provides many advantages such as shape forming, finer particles in the final products without using any grain refiners such as Pt, CeO etc., reduced macro defects, etc [18-20]. Recently, we investigated the effect of the addition of nanometer-sized inclusions on bulk YBCO superconductors [21-22]. The difficulties encountered in IG processing is detailed these papers. The long term goal is to produce Ag-doped single grained bulk GdBCO superconductors. In the present work, we investigated the effect of different time dwells on the growth sectors of Ag-doped GdBCO bulk composites. the utilization of bulk LREBa$_2$Cu$_3$O$_{7-\delta}$ (LREBCO or LRE-123, light rare earth elements such as Y, Nd, Sm, Gd, etc,) superconductors in various scientific and technological applications are increased due to their high trapping magnetic fields compared to conventional best magnets available in market. Producing single grained Ba$_2$Cu$_3$O$_{7-\delta}$ (GdBCO or Gd-123) bulks are important in various scientific and technological applications. Compared to YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO or Y-123) there is a chance to form a small fraction of solid solutions in GdBCO which helps in flux pinning. These solid solutions are of the order of nanometric size and effectively pins the flux at higher fields [1-6].

2. Experimental details

![Figure 1](image)

**Figure 1.** Thermal cycles employed for isothermal growth experiments for all GdBCO-Ag composites. In thermal cycle, X represents the temperature at which dwelled.

The precursor powders of Gd-211 and liquid phases are synthesized using the conventional solid state route. For this, raw materials Gd$_2$O$_3$, BaO and CuO are mixed for several hours and the mixture is then sintered at different temperatures, i.e., at 840 °C, 860 °C and 880 °C, respectively. After each sintering, the powders are grinded mechanically for thorough mixing. The phase purity of all the precursor powders is confirmed with X-ray diffractometer. 20 wt.% of Ag$_2$O is added to the Gd-211 precursor powder and mixed into intimate mixture using a mill with electric motor. The 123 and mixture of
211+Ag$_2$O phase powders are pressed into pellets using a uniaxial press. As discussed in the earlier section, the addition of 20 wt.% of Ag$_2$O reduces the peritectic temperature of GdBCO bulk superconductors and enables to process the material at ~30 °C lower than the actual peritectic temperature, i.e., 1030 °C. Therefore, we aimed to perform the growth at a temperature window of 983 °C to 993 °C. The heat treatment schedules utilized for processing all the bulks are described in fig. 1. The schematic diagram of the sample assembly employed for IG processing is also displayed in fig. 1. For all the samples, the temperature dwell of 25 h is employed. After processing the Gd-986 bulk composite, oxygenation was carried out at 450 °C to 400 °C for 175 h to assure the superconductivity. During the oxygenation, the bulk LREBCO samples changes the non-superconducting tetragonal phase to the orthorhombic superconducting phase. The measurement of the superconducting critical temperature of the Gd-986 composite is performed employing a Superconducting Quantum Interference Device magnetometer (Quantum Design, Model MPMS7).

3. Results and discussion
The cold seeding method is employed for all the samples in the present study; single crystalline MgO is used as seed. Single grains can be produced by employing two different ways (i) thermal gradient method and (ii) an isothermal method. In the thermal gradient method, the temperature changes constantly throughout the growth process. The crystal growth of the LREBCO bulk composite depends on the temperature window allowed for slow cooling during the growth. In the isothermal growth method, below the peritectic temperature of LREBCO bulk, a constant temperature will be employed. In the present study, isothermal growth method is used for understanding the heating cycles to be exploit the IG processing of GdBCO-Ag system. The photographs of the as processed bulk GdBCO composites by different dwells are presented in figs. 2 (a)-(f) for Gd-983, Gd-985, Gd-986, Gd-990, and Gd-992, respectively. MgO seed is employed for all the composites for epitaxial growth, but self-nucleation can be observed in all the samples. Clear growth sectors can be realised in Gd-986 composite. Tuning the heating parameters can produce single grains in Ag doped GdBCO bulks.

![Figure 2](image-url.com)
The isothermal dwell time of 25 h is employed at different temperatures to explore at which temperature the growth is starting. It is well known that the growth rate of the LREBCO is about ~ 0.2 mm/h at the growth parameters considered here. The growth sector is small due to the small temperature window, through which full single-grain GdBCO composites cannot be processed. The present work confirms that the slow cooling through 986 °C would produce single grains of Ag-doped GdBCO bulk superconductors. For that reason for further superconducting investigations, we have chosen Gd-986 composite.

The critical temperature of the Gd-986 composite is measured through the temperature dependence of the ac susceptibility ($\chi(T)$) and the plot is shown in fig. 3. The onset of $T_c$ is found to be 93.6 K with a transition width of 4 K in $\chi(T)$ curve which represents the formation of a small fraction of solid solutions of the type Gd$_{1-x}$Ba$_{2+x}$Cu$_3$O$_7$-$\delta$. The field dependence of the critical current density of Gd-986 superconductor is calculated using the extended Bean critical state model and the curve is displayed in fig 3 (b). The self-field $J_c$ of 16.5 kA/cm$^2$ is achieved for bulk GdBCO superconductor which is doped with 20 wt.% Ag. Extensive microstructural and magnetic studies are underway to investigate the reasons behind the suppression of the $J_c$ curve.

The formation of a large fraction of solid solutions in Gd-986 sample can be attributed to the employment of less time for the peritectic reaction. It is noteworthy to mention here that allowing enough time i.e., a constant thermal gradient for peritectic reaction may result a high quality bulk GdBCO-Ag superconducting system. With these inputs, the mass production of GdBCO-Ag bulks can be carried out. The mass production of bulk LREBCO superconductors is a hot topic in recent applications due to the dramatic increase of the use of these materials in various fields.

4. Conclusions
The isothermal growth of the bulk GdBCO superconductors were investigated in the temperature window of 983 °C to 992 °C with the addition of 20 wt.% of Ag. For all the samples, 25 h dwell time is employed. Large epitaxial growth is observed in GdBCO sample dwelled at a temperature of 986 °C. The employment of the single crystalline MgO seed resulted in multi-nucleation in all the composites. The magnetic measurements on oxygenated GdBCO bulk composite show superconducting nature with an onset of $T_c$ at 93.5 K and a self-field $J_c$ of 16.5 kA/cm$^2$ at 77 K.

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