Journal of the European Ceramic Society 38 (2018) 5036–5042

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original article

Quantification of the level of samarium/barium substitution in the Ag-$Sm_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ system

Wen Zhao*, Yunhua Shi, Difan Zhou, Anthony R. Dennis, David A. Cardwell

Bulk Superconductivity Group, Department of Engineering, University of Cambridge, United Kingdom

ARTICLE INFO

Keywords:
Superconductor
Perovskites
Rare-earth
Electron Probe Micro-Analysis (EPMA)

ABSTRACT

The high-temperature $SmBa_2Cu_3O_{7-\delta}$ (Sm-123) superconducting system, which is characterised by a high critical transition temperature (T_c) and a high critical current density (J_c), suffers severely from the effects of Sm/Ba substitution in the superconducting Sm-123 phase matrix, and especially so for large, single grains grown in air, resulting in a significant variation in T_c at different positions within a single grain. As a result, the suppression of Sm/Ba substitution in the $Sm_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ phase matrix (SmBCO, where x represents the Sm/Ba substitution level in the SmBCO system) is critical to achieving good superconducting properties in this material. Here we report the use of Electron Probe Micro-Analysis (EPMA) to investigate, adjust and optimise the composition of mechanically-stabilised standard Ag-SmBCO bulk single grains. We show that the substitution levels within these samples changes linearly within increasing distance from the vicinity of a single crystal seed used to nucleate the single grain growth process. In addition, we identify a constant value of x of −0.080 for the composition-adjusted Ag-SmBCO bulk single grain. This is the first time that the quantification of the Sm/Ba substitution level in the SmBCO system has been measured accurately and directly using EPMA, and suggests clearly that the Sm/Ba substitution can be suppressed effectively in air. This research will provide significant insight into the development of a process to suppress Sm/Ba substitution even further in superconducting SmBCO single grains in the future.

1. Introduction

$SmBa_2Cu_3O_{7-\delta}$ (Sm-123, or SmBCO) is a member of the (RE) $Ba_2Cu_3O_{7-\delta}$ (RE-123) family (where RE is rare earth element or Y) of high-temperature superconductors (HTS). SmBCO fabricated in the form of large, single grains by melt processing has significant potential for use in practical applications due to its high critical transition temperature (T_c), high critical current density (J_c), the so-called 'peak effect' characteristic present in its magnetic hysteresis (***M-H***) behaviour in high applied magnetic field and high irreversibility field. SmBCO bulk superconductors are capable of supporting macroscopic currents at temperatures above the boiling point of liquid nitrogen (77 K), and can, therefore, be used potentially in a variety of high field, quasi-permanent magnet applications such as magnetic bearings [1] and flywheel energy storage systems [2]. It is necessary to process SmBCO materials in the form of large, single grains and avoid the presence of grain boundaries, however, if the SmBCO bulk superconductor is to carry large currents on the length scale of the sample, which is essential for the generation of magnetic fields that are much larger than those produced by conventional permanent magnet materials [3]. The growth of superconducting (RE)BCO single grains has been developed systematically over the past 30 years, and processes to achieve the stable growth of large SmBCO single grains has been achieved. In general, however, the processing conditions required for SmBCO bulk superconductors are more complicated than those for $YBa_2Cu_3O_{7-\delta}$ (YBCO), which has been investigated more extensively, due primarily to the high melting temperature of the precursor powders, rapid growth rate, which is difficult to control, and the need to process SmBCO under reduced oxygen partial pressure in order to inhibit the substitution of samarium (Sm) on the barium (Ba) site in the superconducting Sm-123 phase matrix [4]. Reducing the substitution level of Ba by Sm in the SmBCO system in a practical processing environment represents a particular challenge due primarily to the severity of this effect in air, which leads directly to vastly inferior superconducting properties compared even with the properties of YBCO single grains. As a result, extensive research performed worldwide on the suppression of Sm/Ba substitution in SmBCO has identified that the effects of substitution can be reduced by the addition of a small amount of BaO_2 or $BaCuO_2$ to the SmBCO precursor powders prior to melt processing [5]. Although the Sm/Ba substitution can be suppressed to some extent by this technique,

* Corresponding author.
E-mail address: zhaowen0910@hotmail.co.jp (W. Zhao).

https://doi.org/10.1016/j.jeurceramsoc.2018.07.007
Received 20 March 2018; Received in revised form 5 July 2018; Accepted 5 July 2018
Available online 06 July 2018

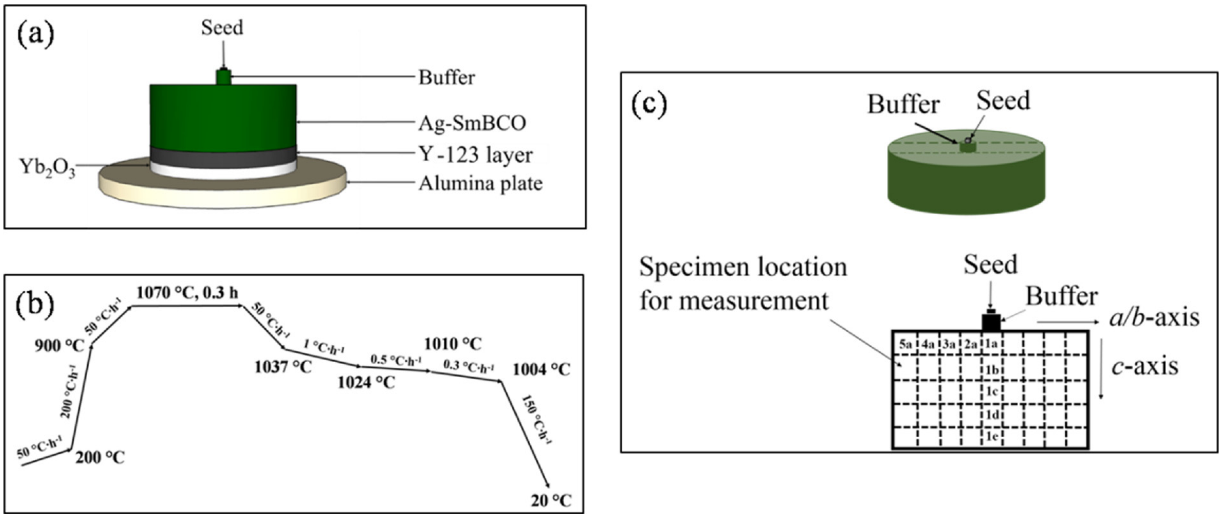

Fig. 1. (a) Schematic illustration of an Ag-SmBCO bulk pre-form with a Y-123 layer prior to TSMG, (b) Schematic illustration of the heating profile used in the TSMG process for the Ag-SmBCO single grains processed with and without a Y-123 layer and (c) Schematic illustration of the sub-sample scheme for the preparation of the SQUID specimens.

the inherent inhomogeneity of the superconducting SmBCO single grains grown subsequently in air limits the effectiveness of this approach, since different amounts of the additional Ba are required throughout the SmBCO single grain growth process to uniformly suppress the extent of Sm/Ba substitution. Furthermore, Sm/Ba substitution occurs in Sm-123 matrix containing embedded, discrete Sm_2BaCuO_5 (Sm-211) inclusions throughout the entire cross section of the sample. As a result, the detectable microscopic length over which the local Sm-123 composition can be measured reliably (i.e. without impingement of Sm-211) is confined, roughly, to 2–10 μm. Beyond that, the Sm/Ba substitution levels at different positions within the single grain are extremely difficult to detect, which presents a significant challenge to energy dispersive x-ray spectrometry (EDX), which is the characterisation technique used most commonly for the characterisation of chemical composition in refractory metal oxides. This is another reason why the precise measurement of the Sm/Ba substitution level in the SmBCO system is rarely possible.

The distribution and extent of Sm/Ba substitution in the SmBCO system has yet to be studied systematically, despite its fundamental influence on the superconducting properties of SmBCO single grains. In this paper, we report for the first time the precise quantification of the Sm/Ba substitution level in the SmBCO system using an Electron Probe Micro-analyser (EMPA). Single grain Ag-SmBCO bulk samples grown by top seeded melt growth (TSMG) with and without the presence of a $YBa_2Cu_3O_{7-\delta}$ (Y-123) layer, added in order to modify the composition to confirm the effectiveness of the method, were measured and analysed systematically as part of this study. The substitution level within the bulk SmBCO samples has been quantified extensively from the top surface to the bottom of the samples, discussed in detail and correlated with the results of their measured superconducting properties, demonstrating unequivocally that EPMA is an effective method for identifying accurately the Sm/Ba substitution level in the SmBCO system. Finally, the addition of a layer of Y-123 at the bottom of the pressed SMBCO pre-forms prior to melt processing leads directly to a more uniform matrix composition in the fully processed SmBCO single grains, which, in turn, results in greater control of the extent of Sm/Ba substitution.

2. Experimental

2.1. Production of Ag-SmBCO single grains in air with and without a Y-123 layer

Commercial Sm-123 (TOSHIMA, average particle size 2–3 μm) and Sm-211 (TOSHIMA, average particle size 1–2 μm) precursor powders in a weight ratio of 3:1, together with 2 wt. % BaO_2 (ALDRICH, purity 95%) to suppress Sm/Ba substitution [5], 1 wt. % CeO_2 (Alfa Aesar, purity 99.9%), to reduce the coarsening of the Sm-211 second phase particles [6] and 10 wt.% of Ag_2O (Alfa Aesar, purity 99+ %, metal basis), to improve the mechanical strength and cracking resistance [7], were mixed thoroughly using a mortar and pestle to yield a net composition of (75 wt. % Sm-123 + 25 wt. % Sm-211) + 2 wt. % BaO_2 + 1 wt. % CeO_2 + 10 wt. % Ag_2O (abbreviated to Ag-SmBCO). The resulting powder was pressed uniaxially into a dark green pellet of diameter 32 mm and thickness 16 mm, which yielded final, as-processed dimensions of 25 mm diameter and 13 mm thickness after a shrinkage about 80% during melt growth. 6 g of commercially available Y-123 (TOSHIMA, average particle size 2–3 μm) and 2 g of Yb_2O_3 (American Elements, purity 99%) to provide an inert layer, were pressed to form a combined supporting pellet using the same size die as the bulk preforms to replace the yttrium-stabilised ZrO_2 rods used commonly to support (RE)BCO samples during melt processing. A generic seed crystal [8,9] was used to nucleate and grow the required grain orientation with an associated buffer layer, the preparation and properties of which are reported elsewhere [10]. At high temperatures, the seed melts partially at its interface with the SmBCO precursor pellet, so contact with the bulk pre-form may lead to contamination of the seeding material and consequently lower the melting temperature of the seed, which results in dissolving and/or the deterioration of the seed. A minimum thickness of 100 μm is required, therefore, for the seed crystal to retain its integrity [11] to avoid such a problem. To further avert the potential of the contaminations from the seed, a buffer layer is additionally added between the generic seed and the Ag-SmBCO perform in this research. The seed, the buffer layer and the Ag-SmBCO pre-form (with and without Y-123 and Yb_2O_3 layers) were aligned before melt processing to yield the required orientation of the single grain, as illustrated schematically in Fig. 1(a). The arrangement was placed on an alumina plate in a box furnace prior to top seeded melt growth (TSMG) using the heating profile shown schematically in Fig. 1(b). The TSMG process is based on a peritectic solidification reaction that occurs at the peritectic temperature, T_p (1045 °C for the starting powder