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$SmBa_2Cu_3O_{6.5}$ seed fabrication for seeded peritectic solidification of $YBa_2Cu_3O_{7-\delta}$

J. C. L. CHOW, J. S. LETTOW, WAI LO, D. A. CARDWELL, H.-T. LEUNG, Y. H. SHI
IRC in Superconductivity, University of Cambridge, Madingley Road, Cambridge, CB3 0HE, UK

The availability of high quality $SmBa_2Cu_3O_{6.5}$ seeds of known orientation is essential for the fabrication of a large grain $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconductor via a seeded peritectic solidification technique. The suitable seed must have a close lattice parameter match to YBCO and a relatively high melting temperature. We report a melt texturing process for the fabrication of $SmBa_2Cu_3O_{7-\delta}$ (Sm-123) seeds using $SrTiO_3$ to control grain nucleation. The physical and structural properties of the seeds were confirmed by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Seeds prepared in this study were used to grow large single grain YBCO superconductors of up to 2 cm in diameter.

1. Introduction

High temperature superconducting (HTS) Y-Ba-Cu-O (YBCO) has significant potential for a variety of engineering applications, such as magnetic bearings, fault current limiters, magnetic clamps and flywheel energy storage systems [1–5]. The flux trapping ability of bulk YBCO, which generally forms the basis of these applications, depends fundamentally on the magnitude and homogeneity of the critical current density, J_c, of the material and the length scale over which it flows [6]. In particular, the presence of grain boundaries and intragrain domains can limit J_c significantly and these are clearly undersirable features of the bulk material. A main processing aim, therefore, is to develop a large grain material with a high J_c that flows over the entire grain geometry. This has been achieved by a variety of peritectic solidification, or melt process, techniques that have been developed over recent years to fabricate large grain YBCO. These techniques have yielded J_c's of up to $10^5\ \mathrm{A\,cm^{-2}}$ at 77 K in grains of typically 1 cm in diameter [7–13].

All YBCO melt processing techniques exploit the peritectic reaction that occurs at around $1010 \pm 10\ ^\circ C$ (the peritectic temperature, T_p) in which $YBa_2Cu_3O_{7-\delta}$ (Y-123) is formed from solid Y_2BaCuO_5 (Y-211), a Ba–Cu–O based liquid phase (L) and oxygen gas (G) [13], i.e.

$$\underset{(\text{Y-211})}{Y_2BaCuO_5} + \underset{(\text{L})}{Ba_3Cu_5O_{6.72}} + \underset{(\text{G})}{0.42O_2} \rightarrow \underset{(\text{Y-123})}{2YBa_2Cu_3O_{6.28}} \quad (1)$$

The Y-211 phase and the liquid in this reaction can be produced by rapidly heating a presintered green body of the desired composition to a temperature well above T_p. Formation of the required Y-123 phase is then achieved by cooling the peritectically molten YBCO sample slowly through the peritectic temperature. It is desirable to add up to 30 mol % of the Y-211 phase to Y-123 prior to melt processing both to generate more flux pinning sites and to prevent loss of liquid during melting [13]. The resulting so-called melt textured growth (MTG) technique typically produces an array of large, well textured but poorly connected grains of the Y-123 phase [3]. This tends to limit the flow of current in the superconducting state to within individual grains; which, in turn, limits the flux trapping ability of the material.

In order to avoid the formation of a granular microstructure and its associated current carrying limitations, it is necessary to control nucleation and growth of YBCO by the use of a seed crystal of a similar lattice constant to the Y-123 phase but with a higher melting point. Such a seeded peritectic solidification technique can be used to grow large single grains of YBCO that do not contain grain boundaries [13, 14]. Application of thermal gradients to the sample during processing may be used to control the seeded peritectic solidification growth process further, although care has to be taken that the "cold point" on the surface of the sample coincides with the position of the seed, otherwise a multigrain sample will be produced.

Single crystal or highly textured seeds within the $(RE)Ba_2Cu_3O_y$ family (RE-123), where RE are rare-earth elements (with the exception of Ce and Tb), are particularly suitable for the growth of $YBa_2Cu_3O_{7-\delta}$ based on structural considerations. Of these, Nd-123 has the highest melting temperature, T_m, of 1085 °C, although this compound is difficult to grow in the form of large single crystals [15]. Sm-123, on the other hand, which has the next highest melting point in this family of compounds at 1060 °C [16], is easier to fabricate in single crystal form and hence is an obvious choice of seed material in this application.

In general the shape, orientation and thickness of the seed significantly influence the microstructure of the melt processed material and, hence, are key variables in the fabrication process [15]. This paper reports the preparation and properties of large area, high quality Sm-123 seeds for the fabrication of large, single grain YBCO via seeded peritectic solidification.

2. Experimental procedure

2.1. Fabrication of metal-textured Sm-123

Analytical reagent (AR) grade powders of Sm_2O_3, $BaCO_3$ and CuO were mixed in appropriate concentrations to yield a net composition of $SmBa_2Cu_3O_y + 0.3\,Sm_2BaCuO_5$. As is the case of Y-123, $SmBa_2Cu_3O_y$ (SmBCO) undergoes a peritectic transition at 1060 °C and the addition of 30 mol % Sm-211 to the Sm-123 precursor is necessary to reduce loss of liquid from the sample prior to crystal growth. This can lead to the formation of pores in the microstructure of the sample [15] and to a change of sample geometry during processing [17–19], both of which are undesirable features of the seed crystal.

The mixed oxide powder was calcined at 1000 °C for 40 h and ground in a yttria stabilized zirconia (YSZ) ball mill for 24 h using methanol as a dispersant. The powder was then oven dried and pressed uniaxially into pellets of 2.5 cm diameter under a pressure of 200 MPa. A single crystal $SrTiO_3$ seed was placed at the centre of the upper surface of the sample prior to processing, in order to maximize the size of the Sm-123 phase domain, and then melted at 1115 °C for 1 h in a horizontal tube furnace under a flowing gas atmosphere of 1 vol % O_2 in nitrogen. Initially the temperature was lowered rapidly to 1045 °C, then slowly at a rate of $0.2\,^{\circ}C\,h^{-1}$ to 1030 °C and finally more rapidly to room temperature. The resultant melt textured Sm-123 sample with the $SrTiO_3$ seed at its centre is shown in Fig. 1. Large grains of Sm-123 are clearly visible in the surface of the sample and there is no evidence of liquid loss during processing.

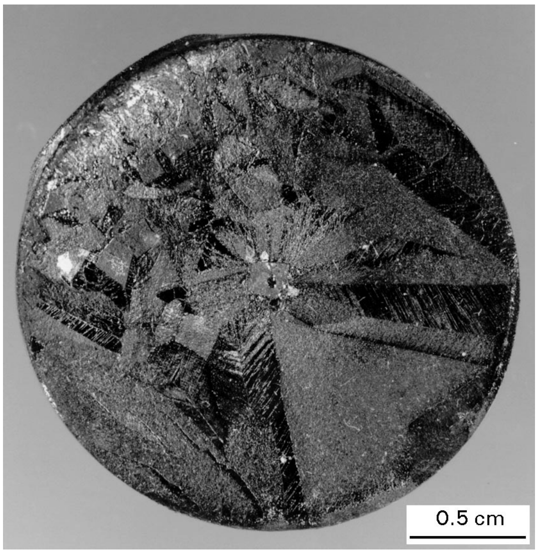

Figure 1 Photograph showing the melt-processed Sm-123 sample fabricated using a $SrTiO_3$ seed.

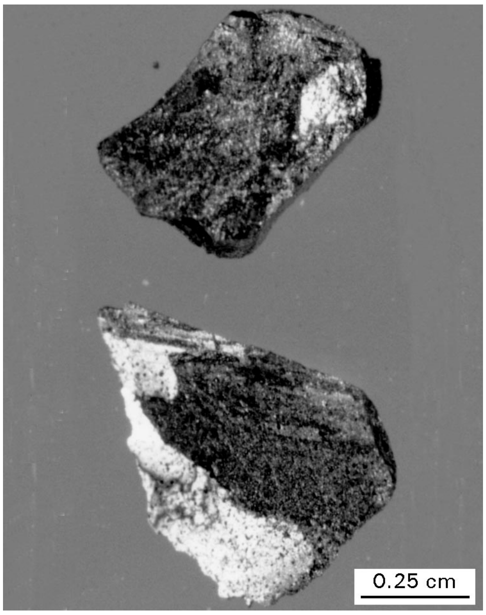

Figure 2 Photograph showing fragments of Sm-123 grains with surface areas of $\sim 1\ cm^2$.

2.2. Processing of Sm-123 seeds

The melt textured Sm-123 sample was placed in an agate mortar and tapped carefully with a pestle to generate microcracks within its microstructure. These tended to form most readily along the *a–b* planes of the RE-123 compounds, which enabled individual plate-like Sm-123 grains to be separated with their thicknesses parallel to the crystallographic *c*-axes. This process produced a number of large, irregularly shaped grains that each exhibited at least one very flat crystal plane surface, as shown in Fig. 2. The orientation of the exposed surface of selected grains was determined by XRD. The grains were then cut parallel to their crystallographic *a–b* planes using a diamond impregnated steel wire and polished to produce smooth surfaces. The melting point of the seed was determined by DTA of its off-cut and its texture confirmed using a Cambridge Stereoscan S250 SEM. Finally the Sm-123 seed was used to grow large single grain YBCO by a seeded peritectic solidification process.

2.3. Seeded peritectic solidification

The seeded peritectic solidification technique used in this study is described in detail elsewhere [13]. Briefly, a Sm-123 seed was placed with its *a–b* plane in contact with the centre of the upper surface of a sintered precursor pellet of Y-123 enriched with 30 mol % Y-211. The pellet was heated to a temperature of 1025 °C, i.e. intermediate between the peritectic temperatures of YBCO and SmBCO, at a rate of $200\,^{\circ}C\,h^{-1}$; cooled at $120\,^{\circ}C\,h^{-1}$ to an isothermal solidification temperature of 985 °C; cooled slowly at $1\,^{\circ}C\,h^{-1}$ to 970 °C, and finally more quickly to room temperature. Further control of grain nucleation and growth was achieved by thermal gradients of up to 15 °C cm^{-1} that were applied to the sample during processing in a purpose-built box furnace that incorporated a cold finger [20]. This process yielded a large grain of rectangular geometry with dimensions up to $2 \times 2 \times 1\ \mathrm{cm}^3$.

3. Results and discussion

YBCO is typically heated to between 20 to 30 °C above its peritectic temperature prior to peritectic solidification to obtain a uniform and thorough decomposition of the Y-123 phase [21–24]. As a result, the melting point of the seed should be at least 1050 °C if it is to remain intact during the melt process. Fig. 3 shows a DTA thermograph for a heating cycle of a typical Sm-123 seed. It can be seen that the peak of the thermograph is sharp and that melting begins at around 1071.4 °C. This is slightly higher than the accepted value of the melting temperature of Sm-123 (~ 1060 °C) and may be attributed to the modified, Sm-211 enriched, initial composition used to prepare the seed. The melting point of the second is significantly higher than that of Y-123, however, and therefore suitable for use in seeded peritectic solidification.

A second important consideration in the peritectic solidification process is the orientation of the plane of the seed in direct contact with the surface of the YBCO pellet, which determines the orientation of the melt processed Y-123 grain. Precursor pellets may be formed readily in cylindrical shape and seeded peritectic solidification is usually performed on samples of this geometry. In addition, the Y-123 phase grows most rapidly along the *a* or *b* lattice directions [25], which should coincide with the longer dimensions of the sample for ease of processing, i.e. along the radius of the cylinder in this case. It is necessary to ensure, therefore, that the surface of the Sm-123 seed in contact with the YBCO pellet is orientated as closely as possible to the *a–b* plane. Fig. 4 shows an XRD pattern of a typical Sm-123 seed prepared by melt texturing after cutting and polishing. A strong peak corresponding to the (0 0 4) reflection of the Sm-123 lattice is predominant in this figure, which indicates that the seed is orientated primarily with its *c*-axis parallel to its thickness; as required for peritectic solidification. The presence of the smaller peaks in Fig. 4, however, suggests that other crystal planes may also be present in the surface of the sample in smaller relative proportions and it was necessary to investigate the texture of surface of the seed further using SEM prior to melt processing.

The microstructure of the surface of the seed is shown in Fig. 5. Fig. 5a shows the texture of the surface of the seed under relatively low magnification. It is clear that this exhibits a textured, flake-like microstructure and incorporates individual grains that are believed to be particles of Sm-211 [26]. The presence of both features is confirmed by the higher magnification micrograph shown in Fig. 5b. Any variation in orientation in the surface of the Sm-123 seed could lead to the nucleation of a grain along a non-*a–b* crystallographic plane during the solidification process, although no direct evidence of this can be gleaned from these micrographs. Unfortunately, it is extremely difficult and time consuming to grow sufficiently large Sm-123 single crystals of the quality required to eliminate any ambiguity in seed orientation [27, 28]. Preparation of seed crystals by a melt-process technique method, on the other hand, has the clear advantages of speed, simplicity and ability to produce a large seed although the reproducibility of subsequent peritectic solidification may be lower than that achieved for single crystal seeds. This has not proved to be a significant limitation in this study, however, given the predominance of the *a–b* plane texture in the surface of the seed and a melt texture process has proved adequate for the preparation of seeds for peritectic solidification of YBCO.

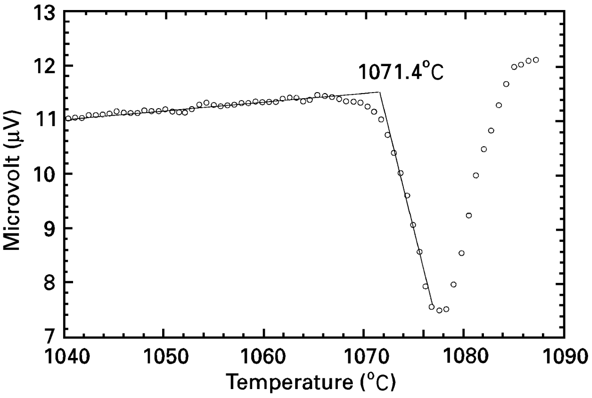

Figure 3 DTA thermograph of a Sm-123 seed.

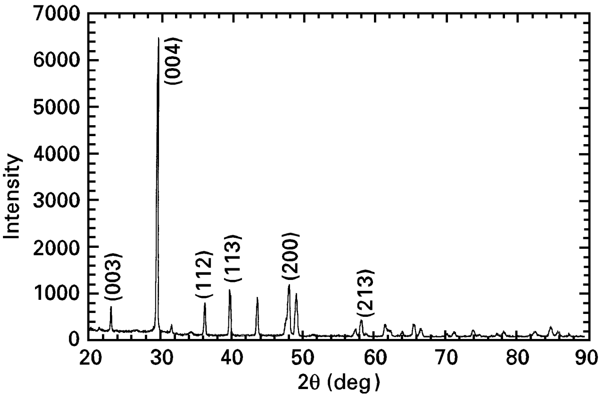

Figure 4 XRD trace of the Sm-123 seed showing a strong (0 0 4) peak.

The nucleation of individual grains will occur first at the coolest region in the molten YBCO precursor pellet if the specimen is cooled in the presence of a temperature gradient. This temperature minimum occurs at the tip of the cold finger in the thermal gradient furnace used in the present study [20]. Consequently, it is necessary to position the specimen in the furnace so that the location of the Sm-123 seed on the surface of the sample coincides with this thermally driven nucleation site in order to produce a single grain material. The required growth conditions are more likely to be achieved if a large area seed is used, therefore, in view of the uncertainty of the point of

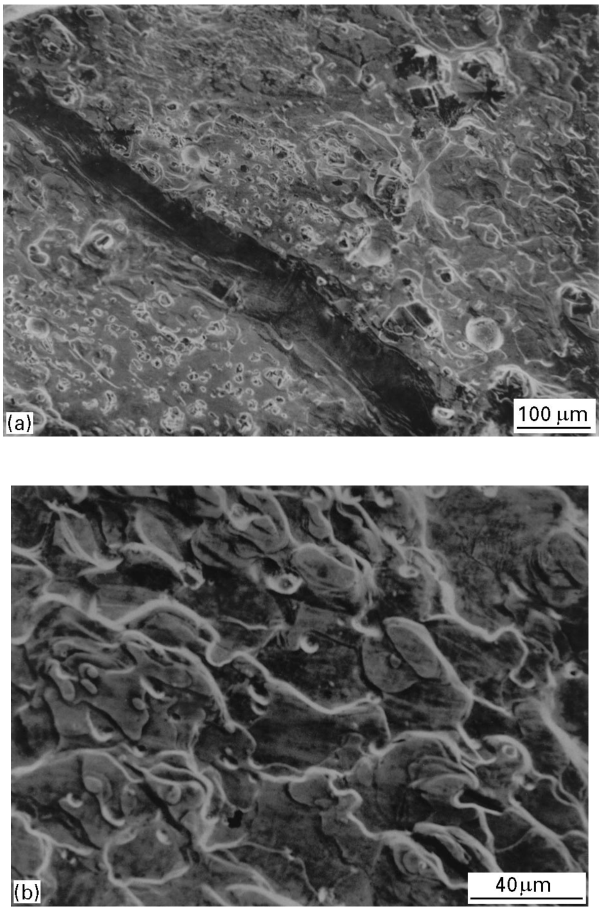

Figure 5 (a) Low and (b) high magnification SEM micrographs of the surface of the Sm-123 seed.

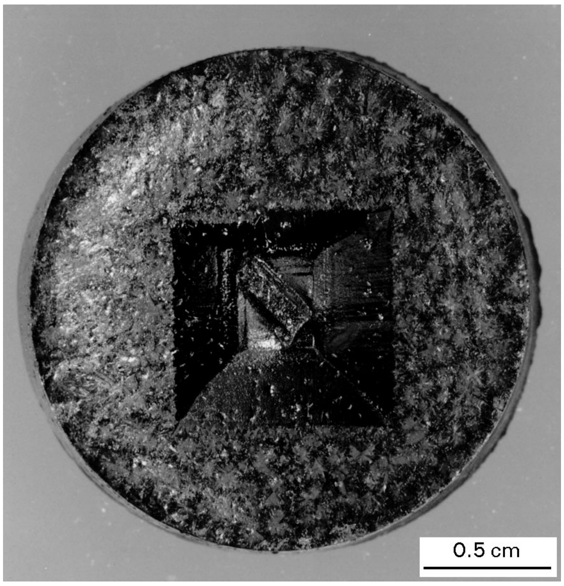

Figure 6 Photograph showing a large YBCO grain fabricated using a large area melt processed Sm-123 seed by slow cooling from 985 °C for 150 h.

lowest temperature at the surface of the sample (known typically only to within an accuracy of a few millimetre). A feature of the present fabrication technique is that it produces seeds of sufficiently large area ($\sim$ 50 mm^2) to overcome this potential processing difficulty. It should be noted, however, that the use of a large area seed may lead to secondary grain nucleation along a non-desired crystallographic orientation away from the centre of the seed. This effect is inhibited in the present study, however, by the use of sharp thermal gradients during processing.

Fig. 6 shows a photograph of a large, single grain of YBCO with 0.1 wt % Pt doping fabricated by peritectic solidification. This sample was grown in 150 h by slow cooling from 985 °C using a seed prepared by the melt process technique described above. The advantages associated with the addition of Pt to the precursor powder and its effect on the microstructure of the fully melt processed material, which are outside the scope of this paper, are discussed in detail elsewhere [29, 30].

4. Conclusions

A high quality, large area seed is essential for the fabrication of large grain YBCO by seeded peritectic solidification, particularly for processes that use thermal gradients. Sm-123 is the most appropriate seed for this purpose in view of its close lattice parameter match and higher melting point relative to that of the Y-123 phase. Melt processing under the influence of a $SrTiO_3$ seed has been found to be a suitable method of fabricating Sm-123 seeds and offers a much more reliable and expedient method of seed fabrication than conventional single crystal growth techniques.

DTA and XRD measurements have been performed to confirm the physical and structural properties of melt processed Sm-123 seeds required for the fabrication of large grain YBCO. SEM analysis of the seed reveals that its surface consists of a flake-like morphology and incorporates trapped Sm-211 grains. Such a structure, however, appears to provide a satisfactory nucleation site for single YBCO grains and large grain samples have been grown successfully using seeds prepared by this technique. A theoretical study of the interaction between the seed and the YBCO sample during the crystal growth process is underway and will be the subject of a future publication.

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