Nano-composite single grain $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ / $\text{Y}_2\text{Ba}_4\text{CuBiO}_y$ bulk superconductors

N. Hari Babu, Cheng Liu, K. Iida and D. A. Cardwell
IRC in Superconductivity and Department of Engineering, Madingley Road, University of Cambridge, CB3 0HE, UK.

Email: nhb24@cam.ac.uk

Abstract: We have succeeded recently in synthesizing a chemically stable, inert family of materials of composition $\text{Y}_2\text{Ba}_4\text{CuMO}_y$ ($\text{Y}$-$2411$ where $\text{M} = \text{Nb, Ta, Mo, W, Zr, Hf}$) within the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\text{Y}$-$123$) phase matrix that forms effective flux pinning centers of nano-scale dimensions. In this paper we report the synthesis of the $\text{Y}_{2}\text{Ba}_4\text{CuBiO}_y$ phase with nano-scale dimensions that is similarly compatible with the $\text{Y}$-$123$ matrix and which does not impair the properties of the bulk superconductor. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ / $\text{Y}_{2}\text{Ba}_4\text{CuBiO}_y$ precursor powders enriched with various amounts of $\text{Bi}_2\text{O}_3$ and $\text{Y}_2\text{Ba}_4\text{CuBiO}_y$ have been fabricated successfully in the form of large, single grains by the top seeded melt growth (TSMG) process. Microstructural studies of these composites reveal the presence of nanometer-sized $\text{Y}_2\text{Ba}_4\text{CuBiO}_y$ and much larger $\text{Y}$-$211$ phase particles ($\sim 1$ $\mu$m) embedded in the $\text{Y}$-$123$ phase matrix. The critical current density of the nano-composites is observed to increase significantly compared to undoped YBCO.

1. Introduction
The critical current density, $J_c$, of bulk, single grain melt processed $\text{Y-Ba-Cu-O}$ (YBCO) is $\sim 20$-$40$ KA/cm$^2$ at 77 K and at 0 T, which is nearly two orders of magnitude lower than that achieved in thin films or coated conductors of similar composition. In order to achieve higher trapped magnetic fields in bulk materials, therefore, it is necessary to increase $J_c$ further. The size of defects in the bulk superconducting matrix, which are responsible for flux pinning, should be typically twice the size of the coherence length (a few nano-meters in YBCO) to optimize the flux pinning force. To date the defect density in melt processed (RE)-Ba-Cu-O bulk superconductors has been engineered partially by refining the size of RE$_2$BaCuO$_5$ (RE-$211$) second phase inclusions in the bulk matrix and by increasing their density [1,2]. RE-$211$ particles, however, tend to ripen during the REBa$_2$Cu$_3$O$_{7-\delta}$ (RE-$123$) peritectic solidification process [3], and, as a result, refining the size of these inclusions on the nano-scale has generally proved unsuccessful. Weinstein et al [4] have introduced U-containing 300-400 nm particles as second phase inclusions into bulk YBCO. The chemical composition of these U-phase particles has been identified as $\text{Y}_2\text{Ba}_4\text{CuUO}_y$ [5] and their presence has been demonstrated to contribute significantly to enhanced flux pinning in the bulk material [4,6]. The $\text{Y}_2\text{Ba}_4\text{CuUO}_y$ phase has subsequently been synthesized separately via a solid state reaction process and introduced into the Y-$123$ superconducting matrix in the form of sub-micron inclusions [7]. More recently, Hari Babu et al [8,9] have demonstrated that the U-element in the $\text{Y}_2\text{Ba}_4\text{CuUO}_y$ phase can be replaced with Zr, Hf, Nb, Ta, Mo and W. These new phase particles are observed to exhibit very important properties...
both during and post melt processing [10]. Specifically, they form nano-scale (10-20 nm) inclusions in the RE-123 matrix that are chemically stable with the Ba-Cu-O liquid, have a negligible affect on Tc of the parent superconductor and, finally, do not ripen at elevated temperature during melt processing. The distinct nature of these particles has made it possible to engineer the microstructure of bulk (RE)BCO superconductors on the nano-scale for the first time. In this paper, we report the synthesis of Y2Ba4CuBiOy phase powder and, subsequently, large, single grain Y-123/Y-211/Y2Ba4CuBiOy nano composites by TSMG process from precursor pellets enriched with Bi2O3 and Y2Ba4CuBiOy that exhibit high critical current densities.

2. Experimental

Y2Ba4CuBiOy phase powders were prepared from pure (99.9%) Y2O3, BaCO3, CuO and Bi2O3 precursor powders using a solid-state reaction process. The powders were mixed initially using a mortar and pestle and then calcined repeatedly between 900 – 1050 °C with intermediate grinding. Finally, the synthesized Y2Ba4CuBiOy powders were mixed with Y-123 and Y-211 phase powders in the appropriate molar ratios for the following compositions:

(1) Y-123 + 0.1wt% Pt + x wt% Bi2O3; x = 0, 5, 10, 20.
(2) Y-123 + y mol% Y2Ba4CuBiOy + 0.1wt% Pt; y = 2.5, 5, 10, 15, 20, 30.
(3) Y-123 + 10 mol% Y-211 + z mol% Y2Ba4CuBiOy + 0.1 wt% Pt; z = 5, 10, 20 and 30.

Small, melt-textured Nd-Ba-Cu-O crystals were used as seeds in a TSMG melt process and a continuous slow cooling method was employed for all the samples fabricated in this study [6]. The microstructural features of the samples were investigated by polarised light microscopy. Samples of all compositions were annealed after melt processing in flowing O2 gas at 400 °C for 100 hours. The superconducting transition temperature and critical current density of each sample was measured using a SQUID magnetometer.

3. Results and discussion

Figure 1 shows the XRD pattern (Cu Ka) recorded for the Y2Ba4CuBiOy phase. All the observed peaks can be indexed to a double perovskite, cubic crystallographic structure similar to that of the Y2Ba4CuUOy or Y2Ba4CuWOy phases [5,9]. The (h, k, l) indices are labeled in the figure for each peak. No peaks corresponding to other, known Y/Ba/Cu/Bi/O phases are present in the powder. The

Figure 1. XRD patterns for Y2Ba4CuBiOy powders and a melt processed sample with starting composition Y-123 + 10 wt% Bi2O3.

Figure 2. Tc of single grain, melt processed samples as a function of Y2Ba4CuBiOy content.

Figure 3. (a) Illustration of the top view of a single grain of starting composition Y-123 + 5 wt% Bi2O3 + 0.1wt% Pt. (b) A typical microstructure of a band.
unit cell parameter is measured from this data to be 8.5427 Å. The XRD pattern of a powdered Y-123 + 10 wt % Bi$_2$O$_3$ melt processed pseudo-crystal is also shown in Fig. 1 for comparison. It can be seen that the Y$_2$Ba$_4$CuBiO$_y$ and Y-123 phases are predominant in this pattern, suggesting that the reaction between Bi$_2$O$_3$, Y-211 and Ba-Cu-O takes place during the solidification process and results in the formation of Y$_2$Ba$_4$CuBiO$_y$ phase, in coexistence with Y-123. No change in the position of the peaks corresponding to the Y-123 phase is observed, suggesting further that Y-123 is not contaminated by Bi during melt processing. The XRD pattern of a powdered melt processed pseudo-crystal with initial composition Y-123 + 20 mol% Y$_2$Ba$_4$CuBiO$_y$ (not shown in fig. 1) also reveals the presence of predominantly the Y$_2$Ba$_4$CuBiO$_y$ and Y-123 phases, suggesting that the Y$_2$Ba$_4$CuBiO$_y$ phase remains stable during the solidification process.

The onset of the superconducting transition temperature for samples with starting composition 2 (i.e. $y = 2.5, 5, 10, 15, 20, 30$) was obtained as a function of temperature in the presence of a 2 mT applied magnetic field from the magnetic moment measured by SQUID magnetometry. Fig. 2 shows the onset $T_c$ as a function of Y$_2$Ba$_4$CuBiO$_y$ phase content in the melt processed YBCO samples. It can be seen that no significant change in $T_c$ is observed with varying Y$_2$Ba$_4$CuBiO$_y$ content, confirming the observation from XRD that Bi from the Y$_2$Ba$_4$CuBiO$_y$ phase does not substitute into the Y-123 lattice during melt processing.

The top view of a single grain sample with starting composition Y-123 + 5 wt% Bi$_2$O$_3$ is illustrated schematically in Fig. 3(a). Approximately periodic bands of second phase inclusions (SPIs) form throughout the grain. A similar microstructure is observed in compositions 1 in the present study and in samples enriched with Nb$_2$O$_5$ in a previous study [11]. Each band is characterized generally by the presence of three distinct regions. Initially, close to the seed crystal, the Y-123 matrix is observed to contain no SPIs. A narrow channel (maximum width 10 μm), consisting mainly of very small (50-300 nm) second phase inclusions trapped in the solid matrix and in voids, then forms at a distance of a few microns from the seed. These SPI’s consist mainly of the Y$_2$Ba$_4$CuBiO$_y$ phase (evidence for the formation of this phase can be seen from the XRD results, shown in Fig. 1) and their size is on the nano-scale. The chemical composition of the solid matrix in this region is predominantly Y-123, with Y$_2$Ba$_4$CuBiO$_y$ nano phase inclusions, Ba-Bi-O phase clusters and a CuO-rich liquid. A layer consisting of a relatively homogeneous distribution of SPIs in the Y-123 matrix follows forms a third band. No CuO or voids are observed in this region and the SPIs consist mainly of the Y$_2$Ba$_4$CuBiO$_y$ phase and a very small quantity of Y-211 particles. A typical microstructure of the band structure in this sample is shown in Fig. 3(b).

The microstructure of YBCO enriched with Y$_2$Ba$_4$CuBiO$_y$ is significantly different to that of samples enriched with Bi$_2$O$_3$. The top view of a single grain sample with starting composition Y-123 + 20 mol % Y$_2$Ba$_4$CuBiO$_y$ is illustrated schematically in Fig. 4(a). Significantly, no band structure,
liquid channels or large cracks are observed in this sample. The microstructures of all samples fabricated with starting compositions 2 are all very similar. The variation of the volume concentration of SPIs (Y$_2$Ba$_4$CuBiO$_y$ and Y-211) along the $a$ and $c$-axes is observed to increase as the crystal growth proceeds due to particle pushing in all samples; only the density of these particles varies from sample to sample, depending on the content of Y$_2$Ba$_4$CuBiO$_y$ in the starting composition. Figure 4b shows a typical microstructure for Y-123 + 20 mol% Y$_2$Ba$_4$CuBiO$_y$. A homogeneous SPI distribution is evident in these microstructures. In addition, large Y-211 particles are present in the Y-123 phase matrices. Obtaining a homogeneous microstructure throughout the single grain is essential if a high, uniform $J_c$ is to be achieved throughout the bulk material, which is fundamental to improved field trapping ability.

Figure 5 shows $J_c$ as a function of magnetic field for samples of Y-123, Y-123 + 20 mol. % Y$_2$Ba$_4$CuBiO$_y$, and Y-123 + 10 mol% Y-211 + 20 mol% Y$_2$Ba$_4$CuBiO$_y$ determined from the width of the hysteresis loop in the measured magnetic moment hysteresis loops. Small specimens were selected ~ 4 mm away from the position of the seed crystal in order to ensure that these contain a large density SPI particles, as shown in Fig. 4(b). It can be seen that $J_c$ at 77 K in the low field regime increases significantly from 5.5 KA/cm$^2$ to 84 KA/cm$^2$ by the addition of nano-phase inclusions. $J_c$ increases further to 112 KA/cm$^2$ with increasing density of SPIs, which is associated directly with the relatively small size of the Y$_2$Ba$_4$CuBiO$_y$ particles. It is important to note that the flux pinning by these nano particles is dominant even at higher magnetic fields, unlike the case of relatively large Y-211 particles. It is anticipated that $J_c$ of bulk YBCO samples processed by TSMG can be improved further by simultaneously increasing the density of the Y$_2$Ba$_4$CuBiO$_y$ second-phase particles and decreasing the size of the Y-211 phase particles in Y-123 superconducting matrix.

4. Conclusions
Y$_2$Ba$_4$CuBiO$_y$ single phase powder has been synthesized and nano-scale (50-300 nm) Y$_2$Ba$_4$CuBiO$_y$ phase inclusions have been introduced successfully into melt processed YBCO for the first time by three different processes without any degradation in $T_c$. These involve (i) melt processing Y-123 precursor powder with Bi$_2$O$_3$ addition, (ii) enriching YBCO precursor powders directly with Y$_2$Ba$_4$CuBiO$_y$ phase particles prior to melt processing and (iii) melt processing Y-123 + 10 mol% Y-211 precursor powder with Y$_2$Ba$_4$CuBiO$_y$. In the first method, approximately periodic bands of SPI-free and SPI-rich regions form throughout the entire single grain. The second and third methods produce a highly homogeneous microstructure containing 50-300 nm sized Y$_2$Ba$_4$CuBiO$_y$ phase particles and a homogeneous distribution of Y$_2$Ba$_4$CuBiO$_y$ nano- and Y-211 phase inclusions, respectively. The critical current density measured from the magnetic moment is observed to increase significantly compared with undoped YBCO to > 10$^5$ A/cm$^2$.

References
[1] Murakami M 1994 Progr. Mater. Sci., 38 311
[2] Cardwell D A 1998 Mater. Sci. Eng. B 53 1
[3] Izumi T, Nakamura Y and Shiohara Y 1993 J. Mater. Res. 8 1240
[4] Weinstein R, Sawh R, Ren Y and Parks D 1998 Mater. Sci. Eng. B, 53, 38.
[5] Hari Babu N et al 2003 Physica C 392 110
[6] Hari Babu N et al, 2002 Supercond. Sci. and Tech. 15, 104.
[7] Cardwell D A, Hari Babu N, Kambara M, Shi Y, Tarrant C D and Schneider KR, 2003 Mats. Sci. Forum, 426, 3499.
[8] Hari Babu N, Reddy ES, Cardwell DA and Campbell AM 2003 Supercond. Sci. Tech., 16 L44
[9] Hari Babu N, Reddy ES, Cardwell DA and Campbell AM, Tarrant C D and Schneider KR 2003 Appl. Phys. Lett., 83, 4806
[10] Cardwell D A, Hari Babu N, Reddy ES, Shi Y 2004 Acta Metallurgica Slovaca, 10, p 31.
[11] Haribabu N, Shi Y, Iida K, Cardwell DA, Haindl S, Eisterer M and Weber H W 2005 Physica C