Growth and superconducting properties of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ single crystals

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Abstract

Single crystals of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ (Bi-2223) have been grown using the travelling solvent floating zone technique in an image furnace. annealing the crystals under high pressures of O$_2$ increased their critical temperature to 109 K, and resulted in sharp superconducting transitions of $\Delta T_c = 1$ K. The superconducting anisotropy of Bi-2223 was found to be $\sim 50$, from measurements of the lower critical field with the magnetic field applied parallel and perpendicular to the $c$-axis. The anisotropy of Bi-2223 is significantly reduced compared to that of Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212), and this accounts for the enhanced irreversibility fields in Bi-2223. Furthermore, Bi-2223 has a higher critical current density, and a reduced magnetic relaxation rate compared to Bi-2212, which are both signatures of more effective pinning in Bi-2223 due to its reduced anisotropy.

1. Introduction

Within the Bi-based family of high-$T_c$ superconductors, the tri-layered Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ (Bi-2223) phase is the most promising for applications, and tapes of this material have already been commercialized [1]. However, unlike the Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi-2212) phase, high-quality single crystals of the Bi-2223 phase are not readily available. This is largely due to the fact that the Bi-2223 phase melts incongruently, and has a complicated multi-phase primary crystallization field [2], which makes it difficult to synthesize single-phase samples of Bi-2223. As a result, previous crystals [3–8] have often contained Bi-2212 intergrowths, which can be detected in magnetization measurements or by high-resolution transmission electron microscopy [7, 8].

The first successful growth of Bi-2223 crystals was only reported in 1994, based on chemical transport in a thermal gradient of molten KCl [3]. These crystals had a $T_c$ of $\sim 105$ K, but were very small ($\sim 0.4 \mu$m thick) and contained spurious phases. Gorina et al [4] were able to grow larger, but still very thin, Bi-2223 crystals with dimensions $1 \times 1 \times 0.003$ mm$^3$ in gas cavities formed in solution melt KCl. The $T_c$ of these crystals was found to be $\sim 109$ K, with a transition width of 3–5 K. However, the crystals were found to contain 3% of the Bi-2212 phase. Small Pb-doped Bi-2223 crystals, which were also 97% pure Bi-2223, were grown by Chu and McHenry using a fused salt reaction of precursors in a KCl flux. These crystals had a $T_c$ onset of $\sim 110$ K but had a very broad superconducting transition [5]. Lee et al [6] also used a KCl flux technique to grow small Bi-2223 crystals, which had rather broad superconducting transitions. The travelling solvent floating zone technique has recently been used to grow large Bi-2223 crystals by Fujii et al [7] and Liang et al [8]. However, these crystals exhibited broad superconducting transitions and contained Bi-2212 intergrowths.

The advantage of the travelling solvent floating zone (TSFZ) technique is that no crucible is involved in the melting and crystallization procedure, which reduces the introduction of impurities into the growing crystal. Furthermore, the crystals grow at one point in the temperature-composition phase diagram, thus allowing the growth of incongruently melting materials. In this paper, we report the growth of large (sizes up to $2 \times 1 \times 0.1$ mm$^3$), pure single crystals of Bi-2223 using the TSFZ technique. By subjecting the crystals to high pressure oxygen annealing, the superconducting transition width is reduced to $\Delta T_c = 1$ K. The second part of this paper focuses on the magnetic properties of the Bi-2223 crystals, and compares them to those of Bi-2212 crystals. We have
measured the superconducting anisotropy of Bi-2223, which is found to be substantially reduced compared to that of Bi-2212. This reduced anisotropy increases the effectiveness of the pinning in Bi-2223, which is reflected in increased critical current densities and irreversibility fields, compared to Bi-2212.

2. Growth of Bi-2223 and Bi-2212 crystals

Travelling solvent floating zone growth of Bi-2223 crystals was performed in a homemade image furnace [2]. Bi-2223 precursor powder was prepared using a sol–gel technique, and was then calcined at 820 °C for 20 h, yielding a mixture of Bi-2212, CuO and traces of Ca$_2$CuO$_3$. This powder was then pressed to form cylindrical ‘feed’ and ‘seed’ rods for the crystal growth. These rods were then mounted inside a vertical quartz tube inside the image furnace, as shown in figure 1.

The feed rod was subjected to a fast pre-melting in order to increase its density, which is crucial for keeping the molten zone stable, and therefore allowing the growth of large crystals. This pre-melting was carried out in a 93% Ar–7% O$_2$ gas mixture, flowing at 0.5 l h$^{-1}$, as was the crystal growth itself. The crystal growth process was then performed by counter-rotating and translating both the seed and feed rods through the molten zone. A very low travelling velocity of 50 μm h$^{-1}$ was used, and the heating power of the furnace was set to give as small a molten zone as possible ($≤3$ mm). The temperature of the molten zone during crystal growth is estimated to be between 920 and 950 °C. An advantage of the image furnace technique is that it produces a very large temperature gradient at the solid–liquid interface (up to 50 °C mm$^{-1}$), which provides a strong driving force to grow large Bi-2223 crystals.

Bi-2223 crystals with typical sizes of 1–2 × 1 × 0.05 mm$^3$ were found inside the seed rod, and grew with their $ab$-planes parallel to the rod’s axis. The as-grown Bi-2223 crystals were oxygen deficient, and were thus significantly underdoped. As is the case with Bi-2212 crystals, the as-grown Bi-2223 crystals required an oxygenation treatment to improve the sample homogeneity and increase $T_c$. Initially, the crystals were annealed under 2 MPa of O$_2$ at 500 °C for 48 h; the zero-field-cooled susceptibility measured in a SQUID magnetometer of these crystals is displayed in figure 2(a). These crystals display $T_c = 111$ K, and a transition width of $\Delta T_c = 5.5$ K. By annealing the crystals under 10 MPa of O$_2$ at 500 °C for 100 h, the superconducting transition becomes very sharp, with $\Delta T_c = 1$ K, as shown in figure 2(b). In this case, $T_c$ of the crystal has been reduced to 109 K, indicating that the crystal is slightly overdoped. These relatively small changes in $T_c$ due to high pressure O$_2$ annealing indicate that the Bi-2223 phase is much less sensitive to oxygen doping compared to the Bi-2212 phase.

The Bi-2212 crystals used in this study were grown by a slow cooling technique in homemade BaZrO$_3$ crucibles; a detailed description of the growth process can be found in [11]. A Bi-2212 crystal with dimensions 2 × 2 × 0.05 mm$^3$ was annealed in air at 500 °C for 100 h. The crystal had a $T_c$ of 87 K and a transition width $\Delta T_c = 1$ K, measured by ac susceptometry.

3. Anisotropy of Bi-2223 crystals

Measurements of the lower critical field ($H_{c1}$) can yield valuable information on the superconducting state of Bi-2223. By measuring $H_{c1}$ with the magnetic field applied parallel to the $c$-axis and then parallel to the $ab$-planes, a measure of the superconducting anisotropy can be obtained. Such an investigation probes the ratio of the $c$-axis penetration depth ($\lambda_c$) to the $ab$-plane penetration depth ($\lambda_{ab}$). Measurements of the temperature dependence of $H_{c1}$ also yield the $T = 0$ K penetration depth, $\lambda(0)$.

The presence of surface and geometrical barriers can impede the entry of flux into high-$T_c$ crystals. If such barriers are present, the SQUID magnetometer will not measure the
equilibrium magnetization, and the first flux penetration field, $H_p$, cannot be identified with the true $H_{c1}$. This effect has been studied in detail in Bi-2212 crystals by Nideröst et al. [9]. They find that, at low temperatures, the pancake vortices creep over the surface barriers; the time dependence of $H_p$ is given by $H_p \approx H_c \exp(-t/T_0)$, where $H_c$ is the thermodynamic critical field and $T_0 = \varepsilon_0 d / \ln(t/t_0)$. Here $\varepsilon_0 = (\Phi_0 / 4\pi \lambda)^2$, $d$ is the interlayer distance, $t$ is the time and $t_0$ is a ‘microscopic time’ scale [10]. We have measured $H_p$ at several magnetic field sweep rates, and have observed this surface creep phenomenon in Bi-2223. The surface barriers do not impede the flow of flux into the crystal if the magnetic field is swept very slowly, at a rate $dH/dt < 1 \times 10^{-4}$ Oe s$^{-1}$ at low temperatures.

Geometrical barriers can be suppressed in crystals which have an elliptical cross-section. As our Bi-2223 crystals are thin platelets, they cannot easily be fashioned into having elliptical cross sections. However, the presence of a geometrical barrier (or a surface barrier) would delay the entry of flux into the crystal and lead to a larger $H_p$ at low temperatures. An upturn in $H_p$ at low temperatures was often observed in early measurements on high-$T_c$ crystals (details can be found in the references of [9]). We find that our measured temperature-dependence of $H_p$ does not show this behaviour, so we can reliably associate $H_{c1}$ with $H_p$ in our measurements on Bi-2223.

The platelet shape of our Bi-2223 crystals leads to a large demagnetization factor when the magnetic field is applied parallel to the $c$-axis. We obtain the demagnetization factor of our crystal by forcing the gradient of the magnetization measured as a function of the applied magnetic field in the Meissner state to be $-1$. For $H \parallel c$ we find a demagnetization factor $N_c = 0.966$ and for $H \parallel ab$ we find $N_{ab} = 0.082$.

The value of the applied magnetic field is then corrected by the demagnetization factor to give the magnetic field at the sample. Figure 3 shows the equilibrium magnetization of a Bi-2223 crystal for $H \parallel c$ and $H \parallel ab$ at $T = 30$ K. The arrows mark the deviation from the linear behaviour of the magnetization in the Meissner state, and therefore mark the lower critical field. A measure of the anisotropy of Bi-2223 is $\gamma = H_{c1}(H \parallel c)/H_{c2}(H \parallel ab) \approx 50$ at $T = 30$ K. This value is between that of extremely anisotropic Bi-2212 ($\gamma = 165$) [11] and YBa$_2$Cu$_3$O$_y$ ($\gamma = 5$–7) [12], and thus Bi-2223 is an interesting material to study the effects of intermediate anisotropy on superconducting properties.

We have measured the lower critical field down to $T = 10$ K and have found the value $H_{c1}(10$ K) $\sim 530$ Oe. Below $T = 10$ K, the pancake vortices creep over the surface barriers at such a low rate that the time taken to perform the experiment becomes unreasonably long. We have therefore extrapolated $H_{c1}$ down to $T = 0$ K. The in-plane penetration depth, $\lambda_{ab}$, is obtained using the expression $H_{c1} = (\Phi_0 / 4\pi \lambda_{ab}^2) \ln \kappa$, where $\kappa$ is the Ginzburg–Landau parameter, which we have assumed to have a value $\kappa = 120$. The $T = 0$ K penetration depth is then found to be $\lambda_{ab}(0) = 1200$ Å. Our choice of $\kappa$ implies that the coherence length is $\xi = 10$ Å; adopting $\xi = 20$ Å leads to $\lambda_{ab}(0) = 1100$ Å. For comparison, the penetration depth in YBa$_2$Cu$_3$O$_y$ is $\lambda_{ab}(0) = 1350$ Å and in Bi-2212, $\lambda_{ab}(0) = 3000$ Å [12].

4. Irreversibility line

A striking feature of Bi-based high-$T_c$ superconductors is the irreversibility line in the $H$–$T$ plane. We have measured the irreversibility line in a Bi-2223 single crystal by acquiring field-cooled (FC) and zero-field-cooled (ZFC) magnetization data using a SQUID magnetometer. Figure 4 shows FC and

**Figure 3.** Upper graph: equilibrium magnetization of a Bi-2223 crystal obtained with the magnetic field applied parallel to the $c$-axis. The magnetic field has been corrected for demagnetization effects due to the platelet shape of the crystal. The deviation from the linear response in the Meissner state marks the lower critical field (indicated by the arrow). Lower graph: equilibrium magnetization of a Bi-2223 crystal obtained with $H \parallel ab$.

**Figure 4.** Field-cooled and zero-field-cooled magnetization of a Bi-2223 crystal at applied magnetic fields ($H \parallel c$) of 1 kOe (squares) and 10 kOe (circles). This data was obtained with a SQUID scan length of 2 cm. The position of the kink at $T \sim 35$ K in the data taken at 10 kOe is independent of the SQUID scan length, unlike the temperature at which the FC and ZFC branches merge. The position of the kink marks the true irreversibility temperature.
Figure 5. Irreversibility lines of Bi-2223 and Bi-2212 crystals displayed as a function of reduced temperature, $T/T_c$, and measured with $H \parallel c$. The irreversibility line of Bi-2223 is translated to higher magnetic fields due to the crystal’s reduced anisotropy. Inset: magnetic hysteresis loop of a Bi-2223 crystal acquired at $T = 40$ K. The second magnetization peak occurs at $H \approx 600$ Oe in Bi-2223.

ZFC data obtained at two different applied magnetic fields using a SQUID scan length of 2 cm. Apart from the merging of the FC and ZFC data, a ‘kink’ can clearly be seen at $T \approx 35$ K in the data taken at $H = 10$ kOe. This kink becomes more pronounced as the SQUID scan length is increased, but always occurs at the same temperature. In contrast, the temperature at which the FC and ZFC curves merge is found to vary by several kelvins as the scan length is changed. This behaviour has been reported in YBa$_2$Cu$_3$O$_7$ single crystals by Schilling et al. By comparing moving sample and stationary sample SQUID techniques, they were able to show that the kink marked the true irreversibility of the crystal. Therefore, we use the position of the kink to trace out the irreversibility line in single crystal Bi-2223.

Figure 5 shows the irreversibility lines (IL) obtained using this method for Bi-2223 and Bi-2212 crystals. The irreversibility lines have been plotted as a function of reduced temperature, $T/T_c$, in order to take into account the different transition temperatures of these two crystals. The graph shows that the irreversibility line of Bi-2223 is translated to higher magnetic fields compared to that of Bi-2212. As the data are presented as a function of $T/T_c$, this behaviour is not due to the higher $T_c$ of Bi-2223. It is well known that the position of the IL is strongly influenced by the anisotropy of the material [12]. Furthermore, as we discuss below, both crystals appear to have similar levels of (weak) disorder, which therefore only has a marginal influence on the IL. Thus, we believe that the observed positions of the IL are due to the different values of the anisotropy we have measured for Bi-2223 ($\gamma = 50$) and Bi-2212 ($\gamma = 165$).

Another interesting feature which can be accessed through magnetic measurements is the occurrence of the second magnetization peak in $m(H)$ loops. This phenomenon has been widely observed in Bi-2212 [14, 15], and is also observed in YBCO, where it occurs at considerably higher magnetic fields [16]. The second magnetization peak (SP) marks the transition of the vortex lattice from the well ordered Bragg–Glass phase toward a highly disordered phase [17]. Its position in the $H$–$T$ plane depends on the competition between the elasticity of the lattice and the amount of disorder in the crystal. Furthermore, the temperature range over which the SP can be observed gives a good indication of the amount of disorder in the crystal [18]. In the inset of figure 5 we show an $m(H)$ loop acquired at $T = 40$ K from a Bi-2223 crystal. We observe the presence of the SP in Bi-2223 at $H_{2nd} \approx 600$ Oe. This is significantly higher than the position of the SP in optimally doped Bi-2212 crystals, which is found to be $H_{2nd} \approx 400$ Oe [14]. This confirms the larger elasticity of the vortex lattice in Bi-2223, which is a consequence of its reduced anisotropy compared to that of Bi-2212. We have also observed that the SP is rapidly suppressed as the temperature increases, and cannot be observed at temperatures above $T = 45$ K in Bi-2223. This behaviour is similar to that of Bi-2212, but differs from that of Pb-doped Bi-2212 [18]; in the latter, the SP can be observed almost up to $T_c$, which is a consequence of the increased amount of disorder in that material. The SP is also observed over a wide temperature range in the disordered superconductor Ba$_{1-x}$K$_x$BiO$_3$ [19]. Thus, the limited extent of the SP in Bi-2223 indicates a lower amount of disorder in these crystals.

5. Critical current density and magnetic relaxation

When comparing the critical current densities ($J_c$) of Bi-2223 and Bi-2212 crystals, it is important to take into account the increased $T_c$ of Bi-2223. As the $T_c$ of our Bi-2223 crystal is $\approx 1.25$ times larger than that of our Bi-2212, we compare Bi-2212 data taken at 10 K (20, 30 K) with Bi-2223 data taken at 12.5 K (25, 37.5 K). The data taken at 30 K on Bi-2212 has the lowest $J_c$ values, and is not labelled on the graph due to lack of space. At each reduced temperature, $T/T_c$, the $J_c$ curves from the Bi-2212 crystal are translated to higher values than those from the Bi-2212 crystal. This shows that the pinning is more effective in Bi-2223.

Figure 6. Comparison of the critical current densities, $J_c$, of Bi-2212 and Bi-2223 crystals. As the $T_c$ of Bi-2223 is $\approx 1.25$ times larger than that of Bi-2212, we compare Bi-2212 data taken at 10 K (20, 30 K) with Bi-2223 data taken at 12.5 K (25, 37.5 K). The data taken at 30 K on Bi-2212 has the lowest $J_c$ values, and is not labelled on the graph due to lack of space. At each reduced temperature, $T/T_c$, the $J_c$ curves from the Bi-2212 crystal are translated to higher values than those from the Bi-2212 crystal. This shows that the pinning is more effective in Bi-2223.
model, and assuming that our platelet-shaped samples can be described as flat discs [11].

For a given reduced temperature, \( T / T_c \), the \( J_c \) values of the Bi-2223 crystal are always higher than those of the Bi-2212 crystal. As the temperature increases, the \( J_c \) of the Bi-2212 crystal decreases much more rapidly, and also presents a poorer magnetic field dependence compared to the Bi-2223 crystal. This shows that pinning is intrinsically more efficient in Bi-2223 than in Bi-2212 crystals.

We have also compared the magnetic relaxation rates of the two crystals, as this measurement is directly related to the underlying pinning potential. We have measured the dynamic relaxation rate, \( S \), using a VSM as described in [11]. The magnetic relaxation rate of the Bi-2212 crystal taken at 20 K is compared to that of the Bi-2223 crystal taken at 25 K in figure 7; these data are at the same reduced temperature, \( T / T_c \), for both crystals. The lower magnetic relaxation is observed for the Bi-2223 crystal, confirming that this crystal has the most effective pinning. This is largely due to the reduced anisotropy of Bi-2223.

6. Summary

We have grown single crystals of Bi-2223 which display sharp superconducting transitions. No indication of Bi-2212 intergrowths were observed in the magnetic measurements. The superconducting properties of Bi-2223 have been investigated through measurements of the lower critical field. Bi-2223 is found to have an anisotropy of \( \gamma = 50 \), which is substantially reduced from that of Bi-2212 (\( \gamma = 165 \)). The irreversibility line of Bi-2223 has been measured, and is translated to higher magnetic fields compared to Bi-2212, which is principally due to the reduced anisotropy of Bi-2223. The reduced anisotropy results in improved pinning properties in Bi-2223, leading to enhanced critical current densities and reduced magnetic relaxation rates.

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References