Growth, microstructures, and superconductivity of Bi$_{2-x}$Pb$_x$Sr$_2$Ca$_{1-y}$GdyCu$_2$O$_{8+z}$ single crystals

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Growth, microstructures, and superconductivity of Bi$_{2-x}$Pb$_x$Sr$_2$Ca$_{1-y}$Gd$_y$Cu$_2$O$_{8+z}$ single crystals

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Bi$_{2-x}$Pb$_x$Sr$_2$Ca$_{1-y}$Gd$_y$Cu$_2$O$_{8+z}$ (x = 0.34 and y = 0.18, 0.34) crystals were grown by the self-flux method. The crystals have a cleavage thickness of only half unit cell up to two unit cells with $T_c$ only dropping 20 K as y is increased from 0.18 to 0.34 for as-grown crystals. However, $T_c$ increased to almost the same value of about 80 K after annealing in air regardless of the Gd doping levels. The co-doping produced enhanced flux pinning compared to the sole Gd doped crystals. A secondary peak effect presented in crystals with x = 0.34 and y = 0.34 was explained by phase segregations containing Gd-rich clusters. © 2004 American Institute of Physics. [DOI: 10.1063/1.1667412]

I. INTRODUCTION

It has been well established that the dimensionality is one of the most important factors controlling the superconducting properties of high $T_c$ superconductors. By reducing the dimensionality structurally and electronically and in turn reducing anisotropy and enhancing coupling between CuO layers has effectively produced improvement of flux pinning in strongly two-dimensional Bi-based superconductors, since the irreversibility field $H_{irr}$ is inversely proportional to $p_c$, the resistivity along the c-axis, and $d_s$, the distance between adjacent CuO planes, i.e., $H_{irr} = 1/(p_c \times d_s)$. Vortex pinning improvement by doping has been proved to be very effective and desirable in a practical viewpoint. It has been well established that all the rare earth (RE) elements can be substituted into the Ca site,$^2$ and all 3d metal ions can be substituted into the Cu site.$^3$ RE doping in the Cu site leading to metal-superconductor transition and accompanying increase of anisotropy are not helpful for the pinning enhancement. However, Pb doping into the Bi sites significantly enhanced flux pinning in Bi2212 crystals.$^4$ We have found that both Y and heavily Pb doping showed improved pinning in Bi2212 single crystals compared to that with sole Y doping.$^5$ Doping with magnetic ions such as Fe and Ni in the Cu site in a slightly level has shown beneficial effects on flux pinning.$^6$ Gd$^{3+}$ doping into Ca positions weakens Josephson coupling and anisotropy also increased in Bi2212.$^8$ Although Gd$^{3+}$ is magnetic, $T_c$ of the Gd doped samples dropped slower than that of Y$^{3+}$ doped samples at the same doping levels. Meanwhile, since Pb doping make the BiO$_2$ layer more conductive and reduces the c lattice parameters,$^9$ it is expected that if the Pb doping was introduced to the Gd doped Bi2212, it could reduce any increase in resistivity along the c-axis that is caused by Gd doping. There may also be a competition between oxygen overdoping induced by Pb and underdoping by Gd$^{11}$. In this paper, we present our results of crystal growth, superconductivity and flux pinning in both Gd and heavily Pb co-doped Bi-2212 crystals. To our knowledge, the Pb and Gd doped Bi2212 have never been reported before.

II. EXPERIMENT

The Pb and Gd co-doped Bi2212 crystals used for the present work were grown using a self-flux method, the same as what we have used to grow both Y and Pb doped crystals.$^5$ High purity Bi$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$, Gd$_2$O$_3$, and CuO were well mixed according to the ratio Bi:Pb:Sr:Ca:Gd:Cu = 2-x:2:2:1-y:y:2 (x < 0.5, y < 0.5) and put into Al$_2$O$_3$ crucibles. The crystal growth was carried out in a horizontal furnace with a large temperature gradient. The sample was first heated up to 1000 °C and held there for about 2–4 h, then fast cooled down to 950 °C (200 °C/h), then slowly cooled down to 830 °C at a rate of 5–20 °C/h, and finally furnace cooled down to room temperature. The real atomic compositions of the resulting crystals were determined by energy dispersive analysis (EDA). Microstructures and phases were determined by using x-ray diffraction (XRD), scanning electron microscope, and atomic force microscope. The as-grown crystals also were annealed in air at 500 °C for 24 h. Superconductivity of the crystals was characterized over a wide temperature range between 5 and 100 K and in various magnetic fields using Physical Property Measurement System (PPMS), Quantum Design.
Interestingly, a strong annealing effect on the similar way to that with sole Gd doping as shown in Fig. 3. x observed for heavily Pb co-doped as-grown samples, the moving towards the oxygen underdoping. For both Gd and doped Bi2212 single crystal samples.8 The decrease of the of Gd doping levels is similar to what was seen in solely Gd doped crystals.8/001 XRD measurements showed that only 0.66:0.34 were determined by EDA for two co-doped sample acted on Bi2212 single crystals.8 However, a clear secondary peak was observed for Pb doped crystals and decreases as Tc/0.34 samples. The weak pinning in the high Gd doping level could be caused by the similar reason that the vortex dimensions transformed from 3D to 2D for high Gd doping levels as observed in sole Gd doped crystals.8 However, a clear secondary peak was observed for the y=0.34 samples at a wide range of temperatures between 20 K and 60 K or 0.25<T<0.65.

The peak effect and peak fields observed in both Pb and Gd (y=0.34) doped samples are much pronounced and much higher than that of sole Gd doped crystals.8 It can be seen from Fig. 5, the peak fields of sole Gd doped samples are almost temperature independent with small values of about 0.18; but Tc increases.4,5,10 The peak effect and peak fields observed in both Pb and Gd (y=0.34) doped samples on both Pb and Gd (y=0.34) doped samples as shown in Fig. 3. As for the possible reasons of the presence of the peak effect in the co-doped samples with high Pb and Gd (y

III. RESULTS AND DISCUSSION

Single crystals obtained have dimensions of up to 2 x 3 mm² in the ab plane for all the doped samples. The real atomic ratios of Bi: Pb=1.64:0.36 and Ca:Gd=0.82:0.18, 0.66:0.34 were determined by EDA for two co-doped sample used in this paper. XRD measurements showed that only (001) peaks can be observed and no extra peaks from secondary phases can be found. SEM observations showed a clear two dimensional growth features for the co-doped crystals as shown in Fig. 1. The crystals were found easy to cleave mechanically. Atomic force image with a line scan of a cleaved crystal was shown in Fig. 2. Cleavage layers are very thin with thickness of only 1.5 nm up to about 5.8 nm. This means that crystals can be cleaved easily at the half unit cell up to about two unit cells. The small values of the cleavage layers indicated that the crystals doped with both Pb and Gd are weakly bonded between layers and therefore exhibited strong 2D features structurally, the same case as that for pure Bi2212 single crystals.

Tc of as-grown samples with sole Gd doping determined by ac susceptibility decreases from 80 to 60 K when x increased from 0 to 0.34. This variation in Tc with increasing of Gd doping levels is similar to what was seen in solely Gd doped Bi2212 single crystal samples.8 The decrease of the Tc was believed to be due to the fact that Gd³⁺ causes samples moving towards the oxygen underdoping. For both Gd and heavily Pb co-doped as-grown samples, the Tc decreased in a similar way to that with sole Gd doping as shown in Fig. 3. Interestingly, a strong annealing effect on the Tc was also observed for x=0.18 and 0.34 samples as shown in Fig. 3.

FIG. 3. Real part of ac susceptibility for different Gd doped Bi1.64Pb0.36Sr2Ca0.66Gd0.34Cu2O8 crystals. y=0.34: as-grown (closed circles), air annealed (open circles); y=0.18: as-grown (closed triangles), air annealed (open triangles).

FIG. 1. SEM image of a Bi1.64Pb0.36Sr2Ca0.66Gd0.34Cu2O8 single crystal.

FIG. 2. AFM images and line scan of a Bi1.64Pb0.36Sr2Ca0.66Gd0.34Cu2O8 crystal surface.
Bi2212 crystals. On increasing oxygen or Pb content, the amount of Bi$^{5+}$ and/or Pb$^{4+}$ (which are smaller than Bi$^{3+}$) increases, and the c-axis parameter decreases resulting in enhanced coupling along the (001) direction. This is supported by the observed decrease of $\rho_c$ and shift of $H_{\text{irr}}$ for high quality Bi2212 crystals with different oxygen doping states ranging from overdoping and optimum to underdoping. By introducing Gd into Ca sites, concentration of hole carriers is depressed due to the injection of electrons by Gd$^{3+}$, similar to that observed in Y$^{3+}$ doped Bi2212, causing an increase of resistivity and anisotropy and in turn reducing the flux pinning since $H_{\text{irr}} \sim 1/(\rho_c \times d_s)$. The peak effect was also weakened or disappeared as the amount of Bi$^{5+}$ cluster units reduced because of the introduction of Gd$^{3+}$. When the amount of Gd$^{3+}$ increased, there is a possibility that the Gd$^{3+}$ ions tend to move together and form Gd$^{3+}$ clusters, or form some ordered cluster networks containing rich Gd$^{3+}$ units. These networks would act the same roles to the vortices as matching effect that has been well accepted as the source of the peak effect in both low and high $T_c$ superconductors.

In summary, both Pb and Gd doped Bi2212 are strongly two dimensional. $T_c$ only dropped 20 K as $y$ increased from 0.18 to 0.34 for as-grown crystals. Annealing significantly move the $T_c$ up to the same values of about 80 K regardless of the Gd doping levels. Both Gd and heavily Pb doping produced enhanced flux pinning compared to sole Gd doping. A pronounced secondary peak effect present in $x = 0.34$ and $y = 0.34$ samples is likely caused by the matching effect due to the formation of networks of clusters containing Gd rich units.

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