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

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

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$\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_{1-y}\text{Gd}_y\text{Cu}_2\text{O}_{8+\delta}$  ( $x=0.34$  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 doping. 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

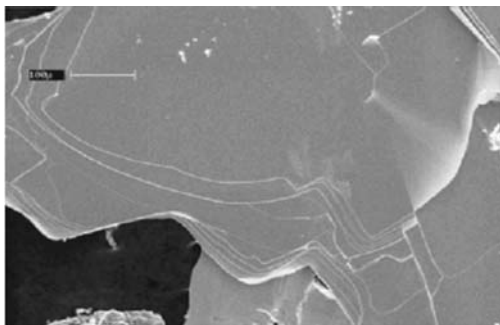
It has been well established that the dimensionality is one of the most important factors controlling the superconducting properties of high  $T_c$  superconductors. By reducing the dimensionality structurally and electronically and in turn reducing anisotropy and enhancing coupling between CuO layers have effectively produced improvement of flux pinning in strongly two-dimensional Bi-based superconductors, since the irreversibility field  $H_{irr}$  is inversely proportional to  $\rho_c$ , the resistivity along the  $c$  axis, and  $d_s$ , the distance between adjacent CuO planes, i.e.,  $H_{irr} \sim 1/(\rho_c \times d_s)$ .<sup>1</sup> 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,<sup>2</sup> and all 3d metal ions can be substituted into the Cu site.<sup>3</sup> RE doping in the Ca 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.<sup>4</sup> We have found that both Y and heavily Pb doping showed improved pinning in Bi2212 single crystals compared to that with sole Y doping.<sup>5</sup> Doping with magnetic ions such as Fe and Ni in the Cu site in a slightly level has shown beneficial effects on flux pinning.<sup>6,7</sup>  $\text{Gd}^{3+}$  doping into Ca positions weakens Josephson coupling and anisotropy also increased in Bi2212.<sup>8</sup> Although  $\text{Gd}^{3+}$  is magnetic,  $T_c$  of the Gd doped samples dropped slower than that of  $\text{Y}^{3+}$  doped samples at the same doping levels. Meanwhile, since Pb doping make the  $\text{BiO}_2$  layer more conductive and reduces the  $c$  lattice parameters,<sup>9</sup>

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  $\text{Gd}^{3+}$ . 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.<sup>5</sup> High purity  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Gd}_2\text{O}_3$ , and  $\text{CuO}$  were well mixed according to the ratio  $\text{Bi:Pb:Sr:Ca:Gd:Cu} = 2-x:2:2:1-y:y:2$  ( $x < 0.5, y < 0.5$ ) and put into  $\text{Al}_2\text{O}_3$  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.

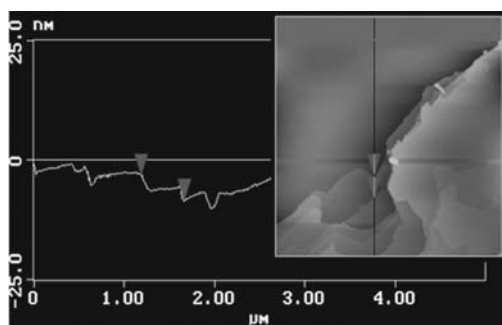
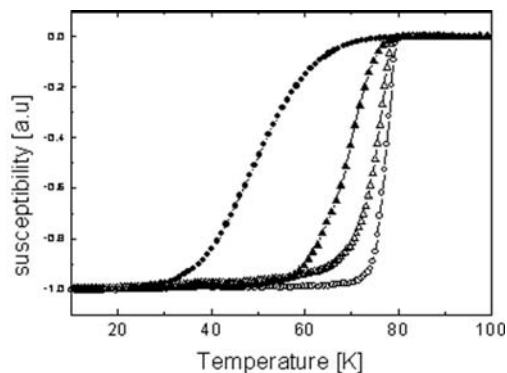
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FIG. 1. SEM image of a  $\text{Bi}_{1.64}\text{Pb}_{0.36}\text{Sr}_2\text{Ca}_{0.66}\text{Gd}_{0.34}\text{Cu}_2\text{O}_{8+y}$  single crystal.

### III. RESULTS AND DISCUSSION

Single crystals obtained have dimensions of up to  $2 \times 3 \text{ mm}^2$  in the  $ab$  plane for all the doped samples. The real atomic ratios of  $\text{Bi}:\text{Pb}=1.64:0.36$  and  $\text{Ca}:\text{Gd}=0.82:0.18$ ,  $0.66:0.34$  were determined by EDA for two co-doped samples 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.

$T_c$  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  $T_c$  with increasing of Gd doping levels is similar to what was seen in solely Gd doped Bi2212 single crystal samples.<sup>8</sup> The decrease of the  $T_c$  was believed to be due to the fact that  $\text{Gd}^{3+}$  causes samples moving towards the oxygen underdoping. For both Gd and heavily Pb co-doped as-grown samples, the  $T_c$  decreased in a similar way to that with sole Gd doping as shown in Fig. 3. Interestingly, a strong annealing effect on the  $T_c$  was also observed for  $x=0.18$  and 0.34 samples as shown in Fig. 3.

FIG. 2. AFM images and line scan of a  $\text{Bi}_{1.64}\text{Pb}_{0.36}\text{Sr}_2\text{Ca}_{0.66}\text{Gd}_{0.34}\text{Cu}_2\text{O}_{8+y}$  crystal surface.FIG. 3. Real part of ac susceptibility for different Gd doped  $\text{Bi}_{1.64}\text{Pb}_{0.36}\text{Sr}_2\text{Ca}_{1-y}\text{Gd}_y\text{Cu}_2\text{O}_{8+z}$  crystals.  $y=0.34$ : as-grown (closed circles), air annealed (open circles);  $y=0.18$ : as-grown (closed triangles), air annealed (open triangles).

$T_c$  of the co-doped samples significantly increased up to about 80 K for both low and high Gd doping levels. This is very different to what have been observed in both Y and heavily Pb doped Bi2212 crystal showing  $T_c$  significantly dropped to as low as 25 K from 80 K at the same doping levels of Gd and Pb.<sup>5</sup> The  $T_c$  variations of the both Gd and Pb doped samples before and after annealing are shown in Fig. 3. It is clear that the Pb doping can easily change samples from oxygen underdoping to optimum doping.

The flux pinning in the Pb and Gd co-doped crystals was investigated by measuring  $M-H$  over a wide temperature range from 5 up to 70 K in fields up to 7 T. At 5 K, both samples exhibited the same pinning behaviors since their  $M-H$  loops overlap at 5 K [Fig. 4(a)]. However, they behave totally different at higher temperatures above 5 K. Figure 4(b) shows  $MH$  loops at 20 K for both samples. It can be seen that  $y=0.18$  sample showed stronger pinning in low field regions than that of  $y=0.34$  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.<sup>8</sup> 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.<sup>8</sup> It can be seen that from Fig. 5, the peak fields of sole Gd doped samples are almost temperature independent with small values of about 400 Oe. The peak effect was absent at  $T/T_c$  above 0.5. In contrast, both Pb and Gd ( $y=0.34$ ) co-doped crystals have a much higher peak fields and the peak effect can persist up to  $T/T_c$  of 0.65. The results of enhanced pinning in these co-doped crystals indicated that Pb did play an important role in reducing the anisotropy and making sample overdoping, in a way that is the same as that observed in either solely or both Pb and Y co-doped Bi2212 crystals.<sup>5</sup> However, the values of peak fields are smaller than in solely Pb doped crystals and decreases as  $x$  increases.<sup>4,5,10</sup>

As for the possible reasons of the presence of the peak effect in the co-doped samples with high Pb and Gd ( $y$

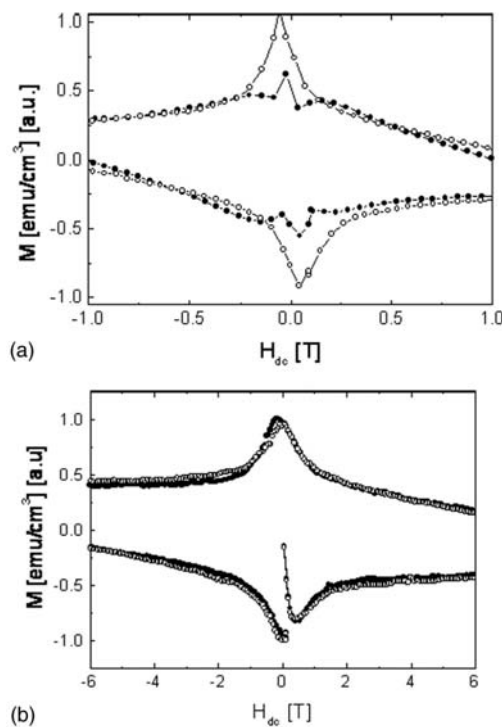


FIG. 4. M-H loops at 5 K (a) and 20 K (b) for air-annealed  $\text{Bi}_{1.64}\text{Pb}_{0.36}\text{Sr}_2\text{Ca}_{1-y}\text{Gd}_y\text{Cu}_2\text{O}_{8+z}$  crystals with  $y=0.34$  (closed circles) and  $y=0.18$  (open circles).

$=0.34$ ) doping levels, we have reported that formation and decomposition of clusters of ionic Bi and/or Pb units in the  $\text{Bi}^{3+}$  2212 matrix, which can be controlled by changing the oxygen or Pb content have been proposed as causes for the appearance of the peak effect in pure or Pb doped Bi2212 crystals.<sup>10</sup> It has been found that the ionic Bi and/or Pb rich clusters of 2212 units, which are sensitive to the annealing or oxygen contents and distribution, exist in pure or Pb doped

Bi2212 crystals.<sup>5,10</sup> On increasing oxygen or Pb content, the amount of  $\text{Bi}^{5+}$  and/or  $\text{Pb}^{4+}$  (which are smaller than  $\text{Bi}^{3+}$ ) 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.<sup>10</sup> By introducing Gd into Ca sites, concentration of hole carriers is depressed due to the injection of electrons by  $\text{Gd}^{3+}$ , similar to that observed in  $\text{Y}^{3+}$  doped Bi2212,<sup>11</sup> 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  $\text{Bi}^{5+}$  cluster units reduced because of the introduction of  $\text{Gd}^{3+}$ . When the amount of  $\text{Gd}^{3+}$  increased, there is a possibility that the  $\text{Gd}^{3+}$  ions tends to move together and form  $\text{Gd}^{3+}$  clusters, or form some ordered cluster networks containing rich  $\text{Gd}^{3+}$  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 are likely caused by the matching effect due to the formation of networks of clusters containing Gd rich units.

## ACKNOWLEDGMENT

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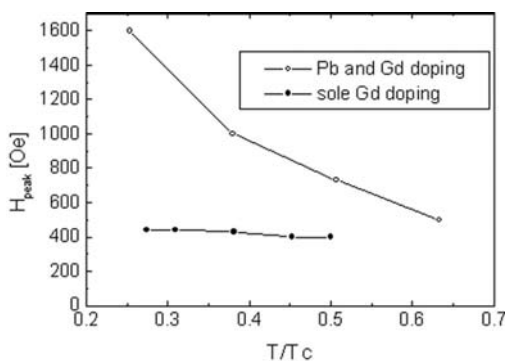


FIG. 5. Secondary peak fields vs  $T/T_c$  for sole Gd (closed circles) and both Pb and Gd co-doped (open circles) crystals. Data for the sole Gd doped crystals were extracted from Ref. 8.

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