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## Superconductivity and flux pinning in Y and heavily Pb codoped Bi-2212 single crystals

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Studies of superconductivity and flux pinning were carried out on  $(\text{Bi}_{1.64}\text{Pb}_{0.36})\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+y}$  ( $x=0, 0.05, 0.11, 0.33$ ) single crystals grown by the self-flux method. X-ray diffraction, transport, and magnetic measurements were performed for purposes of characterization. X-ray analysis revealed that the  $c$  lattice parameter systemically decreases as the Y doping level increases. The superconducting transition temperature  $T_c$  decreases from 80 to 30 K as  $x$  increases. A strong annealing effect on  $T_c$  and superconducting volume has been observed. Resistance measurements show that  $x=0.33$  samples are semiconductive over a wide temperature range between 4.2 and 300 K for the as-grown state, but become metallic with  $T_c$  of 65–70 K after air or oxygen annealing. Flux pinning was studied by measuring the hysteresis loop at different temperatures and different fields. A peak effect was observed in all the codoped samples. Results show that at low temperatures, the peak field is smaller than in solely Pb doped crystals and decreases as  $x$  increases ( $x>0.1$ ). However, the peak field at high temperature for the  $x=0.05$  sample is higher than in heavily Pb doped Bi2212 crystals, indicative of a strong pinning due to the codoping. © 2001 American Institute of Physics. [DOI: 10.1063/1.1356055]

Due to the poor performance of Bi–Sr–Ca–Cu–O high temperature superconducting materials under magnetic fields, an improvement in the flux pinning capability through effective doping is highly desirable. Taking into account the Josephson coupling between CuO layers, Kim *et al.*<sup>1</sup> suggested that the irreversibility field  $H_{\text{irr}}$  is inversely proportional to  $\rho_c$ , the resistivity along the  $c$  axis, and  $d_s$ , the distance between adjacent CuO planes, i.e.,  $H_{\text{irr}} \sim 1/(\rho_c \times d_s)$ . This implies that reducing the  $c$  lattice parameter or increasing the  $c$ -axis conductivity could enhance the flux pinning of a material. It has been well established that all the rare earth (RE) elements can substitute into the Ca site,<sup>2</sup> and all 3d metal ions can substitute into the Cu site.<sup>3</sup> However, most of the doped samples to date have been polycrystalline bulk samples, and the investigators using RE dopants were primary concerned with  $T_c$ , the metal–insulator transition and changes of normal state properties.<sup>2,4,5</sup> A very successful enhancement of the intrinsic pinning, improving  $J_c$  by 2 orders of magnitude over the pure crystals, has already been achieved by Pb doping into the Bi site in the  $\text{BiO}_2$  layer in Bi2212 crystals.<sup>6</sup> A further enhanced flux pinning has been reported in Pb and Cr (in the Cu site) codoped Bi-2212 crystals.<sup>7</sup> No flux pinning investigations have been reported in RE element doped Bi2212 crystals.

$\text{Y}^{3+}$  is the only ion among all the RE elements that is smaller than  $\text{Ca}^{2+}$ . It has been reported that Y doping causes a reduction in the  $c$  lattice parameter.<sup>8</sup> According to the Kim

model,<sup>1</sup> this reduction is likely to be associated with an increase in flux pinning. Unfortunately, no flux pinning investigations have been done on RE-doped Bi2212, except for Y doped crystals which were reported to have strong flux pinning at a 20% doping level.<sup>9</sup> These results have never been replicated, and recent research on Y-doped polycrystalline Bi2212 has indicated that Y doping does not improve pinning, despite Y causing a reduction of the  $c$  lattice parameter.<sup>8</sup> Since Pb doping makes the  $\text{BiO}_2$  layer more conductive and reduces the  $c$  lattice parameter,<sup>10</sup> Pb codoping into the Bi site in the  $\text{BiO}_2$  layer will be introduced into Y-doped Bi2212 in order to further reduce the  $c$  lattice parameter and improve or increase the  $c$ -axis conductivity. It is expected that Pb doping will reduce any increase in resistivity along the  $c$  axis that might be due to Y dopants. Here, we show a detailed study of superconductivity and flux pinning in both Y and heavily Pb codoped Bi-2212 crystals.

The Pb and Y codoped Bi2212 crystals used for the experiment were grown using a self-flux method. High purity  $\text{Bi}_2\text{O}_3$ , PbO,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Y}_2\text{O}_3$ , and CuO were well mixed according to the ratio Bi:Pb:Sr:Ca:Y:Cu = 1.5:0.5:2:1– $x$ : $x$ :2 ( $x \leq 0.4$ ) 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). Structure and lattice parameters

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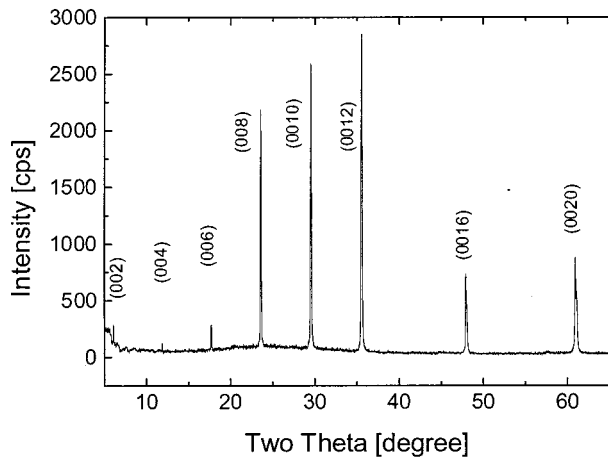


FIG. 1. XRD pattern of a  $\text{Bi}_{1.64}\text{Pb}_{0.36}\text{Sr}_2\text{Ca}_{0.66}\text{Y}_{0.33}\text{Cu}_2\text{O}_{8+y}$  single crystal.

were determined using x-ray diffraction (XRD). The as-grown crystals were annealed at different temperatures in air, argon, and oxygen atmospheres. Superconductivity of the crystals was characterized using standard four-probe transport measurements and ac susceptibility. Flux pinning properties were investigated by the Physical Property Measurement System, Quantum Design.

The single crystals obtained have dimensions of  $1 \times 1 - 4 \times 3 \text{ mm}^2$  in the  $ab$  plane depending on the amplitude of the temperature gradient. The maximum sizes of the Pb+Y codoped crystals are bigger than those grown by the floating traveling solvent zone technique.<sup>6</sup> The real atomic ratios Bi:Pb=1.64:0.36 and Ca:Y=1.95:0.05, 0.89:0.11, 0.66:0.33 were determined by EDA for three codoped samples used in this work. XRD measurements showed that only (001) peaks can be observed and no extra peaks from secondary phases can be found, as shown in Fig. 1. X-ray analysis also revealed that the (008) peak shifts to high angles with increasing Y content (Fig. 2). This indicates that the  $c$  lattice parameters systemically decrease as the Y doping level increases in agreement with the fact that the size of  $\text{Y}^{3+}$  is smaller than  $\text{Ca}^{2+}$ .

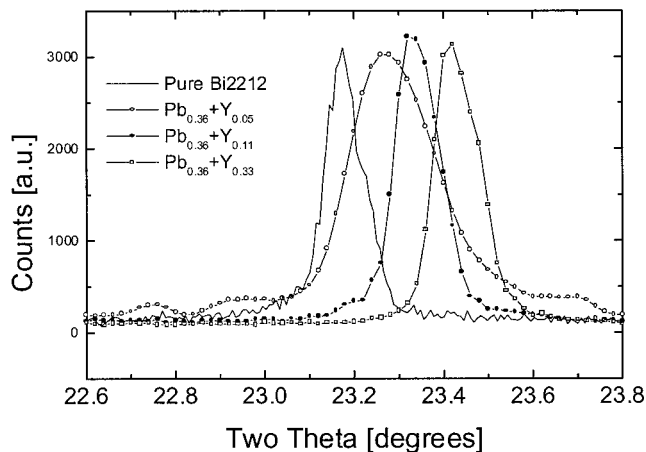


FIG. 2. XRD pattern of (008) peaks for codoped crystals with different Y content.

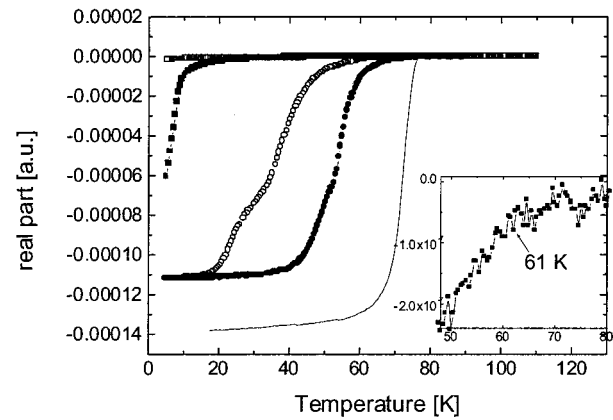


FIG. 3. Real part of ac susceptibility for different Y doped  $\text{Bi}_{1.64}\text{Pb}_{0.36}\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+y}$  crystals [ $x=0.33$ : as-grown (open squares), air annealed (closed squares);  $x=0.11$ : as-grown (open circles), air annealed (closed circles);  $x=0.05$ : air annealed (solid line)].

The transition temperatures  $T_c$  of the codoped crystals are strongly dependent upon the Y doping level.  $T_c$  determined by ac susceptibility decreases from 76 to 25 K as  $x$  increases from 0.05 to 0.3 as shown in Fig. 3. This variation in  $T_c$  with increasing Y is similar to what is seen in solely Y doped Bi2212 polycrystalline samples.<sup>8</sup> A strong annealing effect on the  $T_c$  was observed for  $x=0.11$  and 0.33 samples as shown in Fig. 3. It is clearly seen that the  $T_c$  for the as-grown crystal with  $x=0.11$  shifts about 20 K higher after air annealing, indicative of an oxygen underdoped state in the as-grown crystals. It should be noted that the ac susceptibility for the as-grown crystals with  $x=0.33$  is very small, but becomes larger after annealing in air. This implies that the superconducting volume in this sample is enhanced after annealing. Although the temperature where the major superconductivity occurs in the sample after air annealing is as low as 25 K, the onset is as high as 60 K as shown in the inset. Resistance measurements also show that the  $x=0.33$  sample is semiconductive over a wide temperature range between 4.2 and 300 K for the as-grown state, but becomes metallic with a  $T_c$  onset of 73 K after oxygen annealing, with a  $T_{c0}$  of 30 K (Fig. 4), implying a small superconducting volume above 30 K in agreement with ac susceptibility results.

The flux pinning in the Pb and Y codoped crystals was investigated by measuring  $M-H$  over a wide temperature range from 15 to 70 K. A peak effect can be observed in the codoped samples. However, at low temperatures, the peak field is smaller than in solely Pb doped crystals and decreases as  $x$  increases ( $x > 0.05$ ). The peak effect for  $x=0.05$  starts at 20 K and can persist up to 70 K with the peak fields around 2300 Oe at 20 K, close to what is seen in heavily Pb doped Bi-2212 crystals. Figure 5 shows a series of  $M-H$  loops measured at different temperatures for the  $x=0.05$  sample. This indicated that the codoped crystals have stronger flux pinning than in the solely Y doped Bi2212 samples.<sup>8</sup>

Figure 6 shows peak fields as a function of  $T/T_c$  for the  $x=0.05$  sample. As a comparison, data from a solely Pb doped Bi2212 crystal with the same Pb content as in this

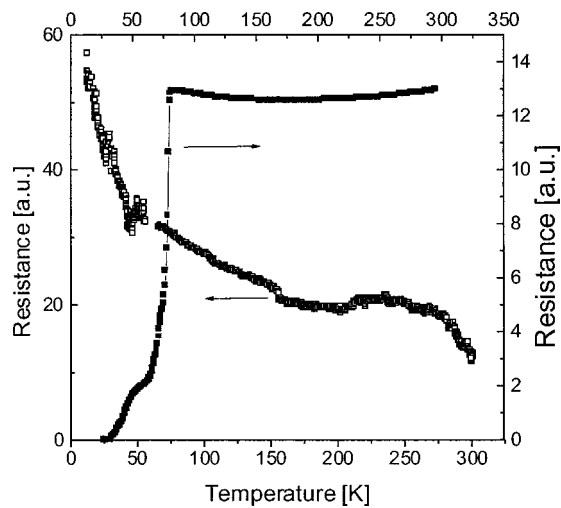


FIG. 4. Resistance vs temperature for a  $\text{Bi}_{1.64}\text{Pb}_{0.36}\text{Sr}_2\text{Ca}_{0.66}\text{Y}_{0.33}\text{Cu}_2\text{O}_{8+y}$  single crystal: (open squares) as-grown; (closed squares) annealed in  $\text{O}_2$  for 24 h.

sample are also shown. It can be seen that the peak effect is present over a wide temperature range  $0.25 \leq T/T_c \leq 0.85$ , behaving the same as in heavily Pb doped Bi2212 crystals. It should be noted that the peak field at high temperatures above  $T/T_c > 0.5$  for  $x = 0.05$  sample is higher than in solely Pb doped crystals, indicative of a strong pinning due to the codoping, even at relatively high fields.

Formation and decomposition of clusters of  $\text{Bi}^{5+}$  and/or  $\text{Pb}^{4+}$  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>11</sup> It is proposed that  $\text{Bi}^{5+}$  and/or  $\text{Pb}^{4+}$  rich clusters of 2212 units, which are sensitive to the annealing or oxygen content and distribution, exist in pure or Pb doped Bi2212 crystals. 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 dop-

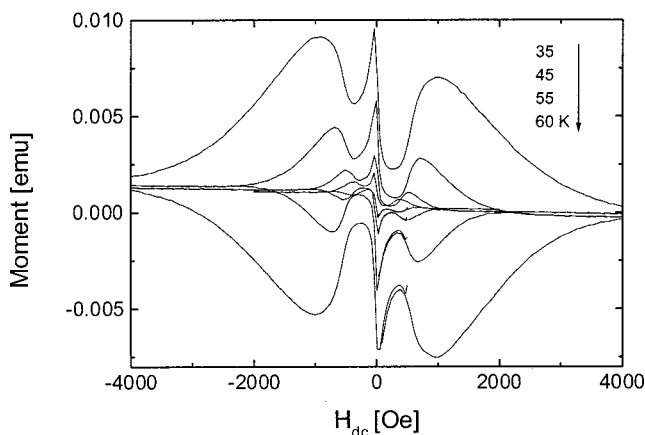


FIG. 5.  $M-H$  loops for  $x=0.05$  crystal at different temperatures.

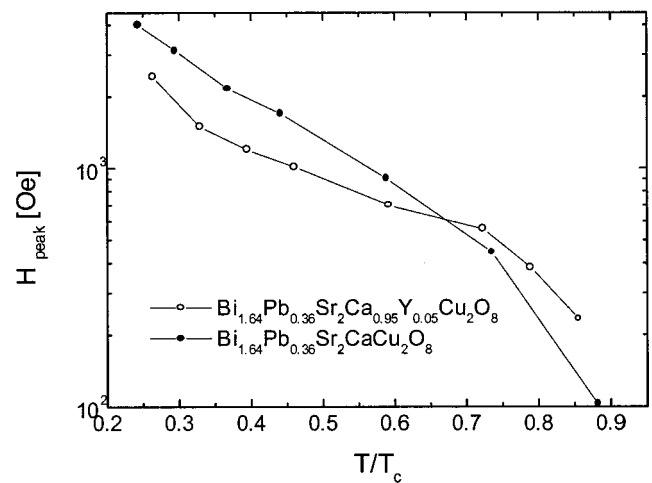


FIG. 6. Peak field vs  $T/T_c$  for heavily Pb (closed circles) and both Pb and Y codoped (open circles) crystals.

ing states ranging from overdoping and optimum to underdoping.<sup>11</sup> The observed reduction in anisotropy in heavily Pb doped Bi2212 crystals<sup>10</sup> also supports our suggestion. By introducing Y into Ca sites, the  $c$ -lattice parameters are further reduced as evidenced in Fig. 2. However, the concentration of hole carriers is also depressed due to the injection of electrons by  $\text{Y}^{3+}$ ,<sup>12</sup> which may increase the resistivity and in turn reduce the flux pinning since  $H_{\text{irr}} \sim 1/(\rho_c \times d_s)$ . Therefore, there must be a competition between the carrier concentration and interlayer interaction that are both induced by  $\text{Y}^{3+}$  doping. It is most likely that the contribution to flux pinning from the decrease in hole carrier concentration caused by  $\text{Y}^{3+}$  is dominant over the contribution from  $c$ -lattice parameter shrinking. However, it is possible that the smaller unit cells due to  $\text{Y}^{3+}$  doping may be more effective as pinning centers at high temperatures compared with the situation in only heavily Pb doped Bi2212 crystals.

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