Properties of Pb-doped Bi-Sr-Ca-Cu-O superconductors

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A zero resistance transition temperature of 108 K has been achieved for Pb-doped Bi-Sr-Ca-Cu-O superconductors prepared by conventional powder solid-state reaction. The materials contained both the high T_c phase ($Bi_2Sr_2Ca_2Cu_3O_x$) and the low T_c phase ($Bi_2Sr_2Ca_1Cu_2O_x$). Critical current density at 100 K in a zero magnetic field was 3.5 A/cm^2 which was larger than that of the Pb-free sample.

The discovery of high-temperature superconductivity in the La-Ba-Cu-O[1] and La-Sr-Cu-O[2] systems was soon followed by the discovery of superconductivity at 90 K in the Ba-Y-Cu-O system.[3] Subsequently high T_c oxide superconductors of the Bi-Sr-Ca-Cu-O system and Tl-Ca-Ba-Cu-O system without any rare-earth elements were discovered by Maeda *et al.*[4] and Sheng and Hermann,[5] respectively. Maeda and co-workers observed a superconducting onset temperature of about 120 K, which was higher than that of $Ba_2YCu_3O_7$ by more than 10 K. However, the transition had a low-temperature tail with a nonzero resistance remaining down to about 75 K. Very recently, Takano *et al.*[6] succeeded in increasing the volume fraction of the high T_c phase by partial substitution of Pb for Bi in the Bi-Sr-Ca-Cu-O system using powders prepared by a co-precipitation method. This letter presents the results of a study in which we have succeeded in sharpening the superconducting transition in a Pb-doped Bi-Sr-Ca-Cu-O system starting from powder reagents. We have measured some properties of this system.

High-purity powders of Bi_2O_3, Pb_3O_4, $SrCO_3$, $CaCO_3$, and CuO were mixed in the molar ratio of Bi:Pb:Sr:Ca:Cu = 0.7:0.3:1:1:1.8. The mixed powders were then calcinated in air at 800 °C for 11 h. This material was reground into powder and pressed into small disks 20 mm in diameter and 0.5 mm in thickness. The pellets were then sintered at 845 °C for two different times (85 and 220 h) in air and subsequently slowly cooled at a rate of about 100 °C/h to 450 °C before being removed from the furnace.

The resistive transition was measured using a standard four-probe technique on a slab sample about 6 mm in width cut from the sintered disk. Voltage and current leads were connected to the samples with silver epoxy. The temperature was calibrated by a carbon-glass resistor. Figure 1(a) shows the temperature dependence of the electrical resistance for sample *A*, which was sintered at 845 °C for 220 h. As the temperature is lowered, the resistance initially decreases almost linearly, which is characteristic of a metal having ohmic behavior. The resistance of this sample first deviates from a linear behavior at a temperature of about 120 K in the same manner as Pb-free samples.[4] With further cooling a sharp drop occurs at about 110 K, with zero resistance being obtained at 108 K. The resistivity at 108 K is estimated to be less than 10^{-6} Ω cm. The transition width, defined at 5 and 95% of the transition height is 10 K. As the measuring current increases from 0.2 to 100 mA, the zero resistance temperature shifts from 108 to 100 K. Figure 1(b) shows the temperature dependence of the electrical resistance for the sample *B*, which was sintered at 845 °C for 85 h. The normal state resistivity of the sample *B* is about twice as large as that of sample *A*. The zero resistance transition temperature with a measuring current of 0.1 mA is 102 K. However, this sample's T_c degrades more rapidly with increasing measuring current due to the formation of a low-temperature tail.

ac susceptibility measurements of bulk samples were also carried out. The Bi-Sr-Ca-Cu-O system, without Pb doping, has two superconducting phases with different T_c of about 105 and 80 K. Those two phases produce a two-step transition in the measurement of temperature dependence of susceptibility.[4,7] However, as shown in Fig. 2, the samples of

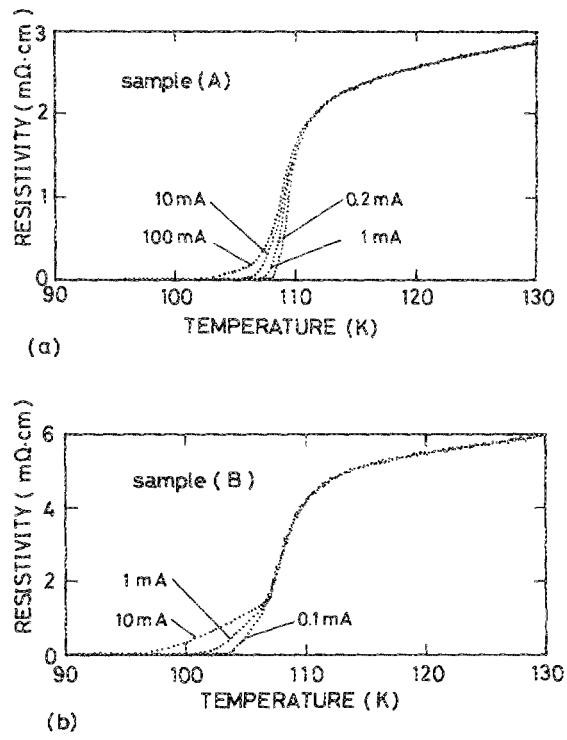

FIG. 1. (a) Temperature dependence of the electrical resistivity for the $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ sintered at 845 °C for 220 h (sample *A*). (b) Temperature dependence of the electrical resistivity for the $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}Cu_x$ sintered at 845 °C for 85 h (sample *B*).

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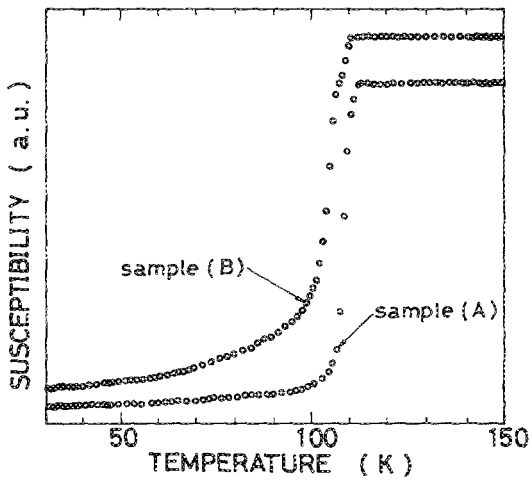

FIG. 2. Temperature dependence of magnetic susceptibility for the $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ sintered at 845 °C for 220 h (sample *A*) and for 85 h (sample *B*).

this work almost have a one-step diamagnetic shift at a temperature corresponding to the transition of high T_c phase. The transition width, defined at 5 and 95% susceptibility drop, of sample *A* is about 10 K, almost corresponding to the width of the resistive transition. Sample *B* has a broader transition, indicating that sintering for a longer time is more effective to obtain a high T_c phase with good quality. Both samples, *A* and *B*, can easily be levitated above a magnet after immersion in liquid nitrogen. This shows a strong diamagnetic flux exclusion at 77 K.

Figure 3 shows x-ray diffraction results of sample *A*, where the circles and crosses indicate the peaks due to the high T_c phase and low T_c phase, respectively. These results show that although the volume fraction of the high T_c phase is greater than that of the low T_c phase, an appreciable amount of low T_c phase is still present in sample *A*. In spite of the coexistence of low T_c and high T_c phases, only one diamagnetic shift was observed. The reason may be due to their microstructural features (i.e., continuous high T_c network). Figure 4 shows an optical micrograph of sample *A*. White rectangular particles are embedded in a dark matrix. Energy dispersive x-ray analysis (EDS) results indicate

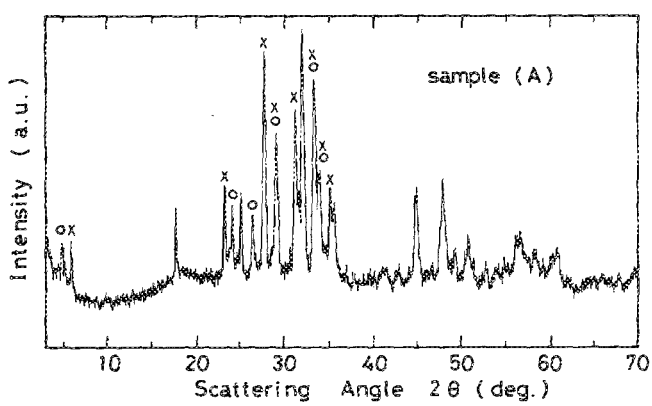

FIG. 3. X-ray diffraction pattern for the $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ sintered at 845 °C for 220 h (sample *A*).

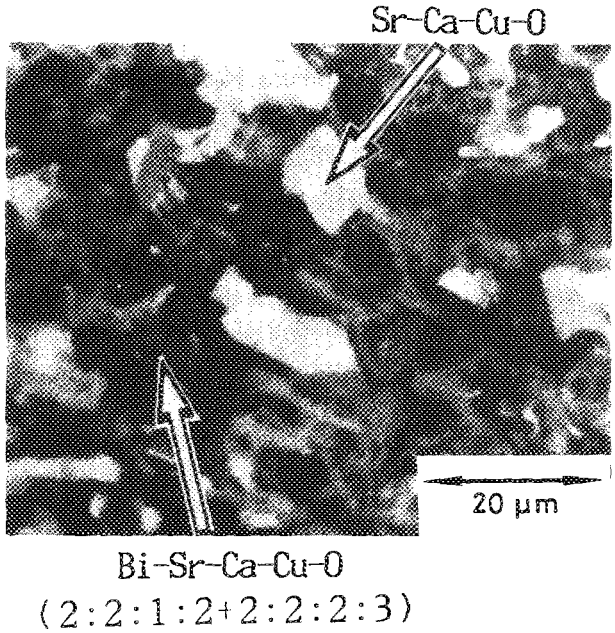

FIG. 4. Optical micrograph of the $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ sintered at 845 °C for 220 h (sample *A*).

that only trace levels of Pb were detected, indicating that most of the Pb vaporized during sintering. EDS results also show that the white particles are Bi-free. These regions are expected to be (Sr,Ca)Cu, oxide compound[7] in a matrix composed of Bi-Sr-Ca-Cu-O systems. The composition of the Bi-Sr-Ca-Cu-O matrix determined by EDS always lies between the stoichiometric compositions of $Bi_2Sr_2Cu_2Cu_3O_x$ (high T_c phase) and $Bi_2Sr_2Ca_1Cu_2$ (low T_c phase). Considering these results along with those of magnetic susceptibility measurements, the most probable microstructure of this two-phase region would have the low T_c phase dispersed in the high T_c phase on a finer scale than the EDS resolving. In addition, the high T_c phase is well connected, giving a superconducting current path throughout the sample in the resistive measurements and shielding

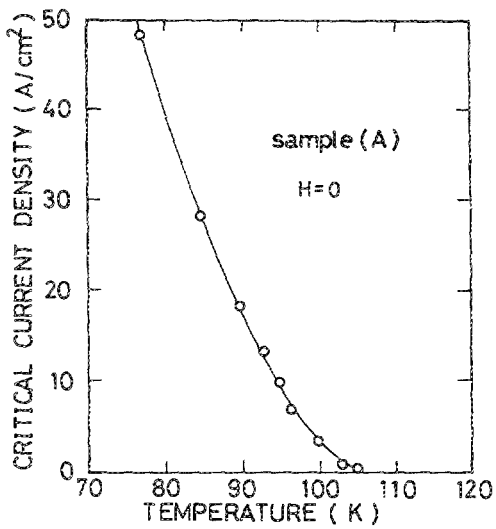

FIG. 5 Temperature dependence of the critical current density for the $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ sintered at 845 °C for 220 h (sample *A*).

of the low T_c phase transition during susceptibility measurement.

Critical current densities J_c were measured in a zero magnetic field by a standard four-probe resistive method. J_c variation with temperature was measured using a temperature-controlled cryostat. Figure 5 shows the temperature dependence of J_c for sample A. As the temperature is lowered, J_c increases rapidly. The J_c values at 77 and 100 K are 48 and 3.5 A/cm^2, respectively. J_c of this Pb-doped sample is larger than that of the Pb-free sample,[8] whose J_c is 1 A/cm^2 at 77 K. However, J_c at 77 K of the Pb-doped sample is still smaller when compared to the typical values of a few thousands A/cm^2 of Ba-Y-Cu-O system.[9] This is probably due to the smaller overall volume fraction of superconducting phases in these samples. This may be related to the coexistence of a nonsuperconducting phase and the relatively low density of our sample (5.7 g/cm^2) compared to the ideal density. Detailed microstructural observations and superconducting properties optimization by longer time sintering and different nominal compositions are now being carried out.

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