Superconductivity in single-phase $Y_1Ba_2Cu_3O_{9-x}$ and thermoelectric power measurement

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Single-phase $Y_1Ba_2Cu_3O_{9-x}$ has been synthesized and characterized. Although x-ray diffraction shows only the $Y_1Ba_2Cu_3O_{9-x}$ phase which has an orthorhombically distorted perovskite structure, resistance measurements reveal two transition temperatures, $T_{c1}=95.5$ K and $T_{c2}=93$ K. Thermoelectric power measurements indicate that $Y_1Ba_2Cu_3O_{9-x}$ is of n type. Strong enhancement and unusual temperature dependence for the "phonon-drag" effect which might be indicative of an unusual superconducting mechanism in this material have been observed.

Since the pioneering work of Bednorz and Müller[1] on La-Ba-Cu-O on superconductivity above 30 K,[2-4] an explosive increase in the highest-known superconducting transition temperature, well above liquid-nitrogen temperature, has occurred in the past few months. Superconductivity above 90 K has been reported by Wu *et al.*,[5] Tarascon, Green, McKinnon, and Hull,[6] and Sun *et al.*[7] in multiphase Y-Ba-Cu-O prepared in many different processes.

Unlike the extensively studied $La_{2-x}M_xCuO_{4-y}$ system (M=Ba, Ca, or Sr), where a tetragonal K_2NiF_4 phase is believed to be responsible for the superconducting properties, it is reported that the superconductivity in the Y-Ba-Cu-O system is due to a $Y_1Ba_2Cu_3O_{9-x}$ oxygen-deficient perovskite structure[8] which has more three-dimensional behavior than the K_2NiF_4 structure.

In this paper, we report synthesis of single-phase $Y_1Ba_2Cu_3O_{9-x}$, resistance measurements, susceptibility measurements, and also the result of thermoelectric power measurements.

Single-phase $Y_1Ba_2Cu_3O_{9-x}$ was prepared by mixing high-purity Y_2O_3, $BaCO_3$, and CuO according to the atomic ratio of [Y]:[Ba]:[Cu] = 1:2:3 following the reported composition of Grant *et al.*[8] The mixed powder was heated at 940 °C in flowing O_2 for 10 h. The fired material was then ground and cold pressed to form a pellet of 1 cm diameter. The pellet was sintered at 970 °C in flowing O_2 for another 10 h. After sintering, the furnace temperature was reduced linearly to 700 °C in 4 h, held at 700 °C for two more hours, and then quench cooled to room temperature by removing the sample from the furnace. The apparent color of the sample prepared, as described above, is black. Under the microscope, however, one can still notice very small amounts of tiny green spots embedded in the black materials as reported by Grant *et al.*[8] We believe the existence of the green spots in our sample is due to incomplete mixing of the powder rather than from the sintering process.

The x-ray diffraction pattern of our sample shown in Fig. 1 reveals only $Y_1Ba_2Cu_3O_{9-x}$, which is of the orthorhombically distorted perovskite structure with lattice parameters $a=3.819$ Å, $b=3.882$ Å, and $c=11.665$ Å, which are very close to the values of Cava *et al.*,[9] who reported an orthorhombic structure with $a=3.822$ Å, $b=3.891$ Å, and $c=11.677$ Å.

Resistivity measurements were performed by the four-probe method using indium pressed contacts on a typical sample size of $1\times1\times8$ mm^3. Typical current density during the resistivity measurement was 0.3 A/cm^2. The effect of testing current density on the transition temperature was unnoticeable for the current density range from 0.1 to 0.5 A/cm^2 in the resistivity measurement. The temperature was measured using a Lake Shore diode and two copper-constantan thermocouples attached to the sample to insure thermal equilibrium between thermometer and sample during the measurement. The accuracy of temperature measurement was within ±0.5 K. Resistivity measurements indicated a superconducting onset temperature of 96 K, a midpoint temperature of 93 K, and complete zero resistance at 91 K. The transition is very sharp with a transition width $\Delta T_c[=T_c(90\%)-T_c(10\%)]=3$ K as shown in Fig. 2. Careful resistivity measurement near the transition region reveals a kink, as if the sample was

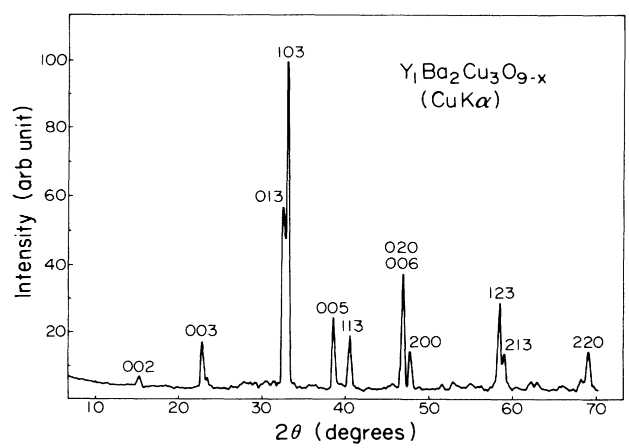

FIG. 1. X-ray diffraction pattern of $Y_1Ba_2Cu_3O_{9-x}$ shows orthorhombic structure with lattice parameters $a=3.819$ Å, $b=3.882$ Å, and $c=11.665$ Å.

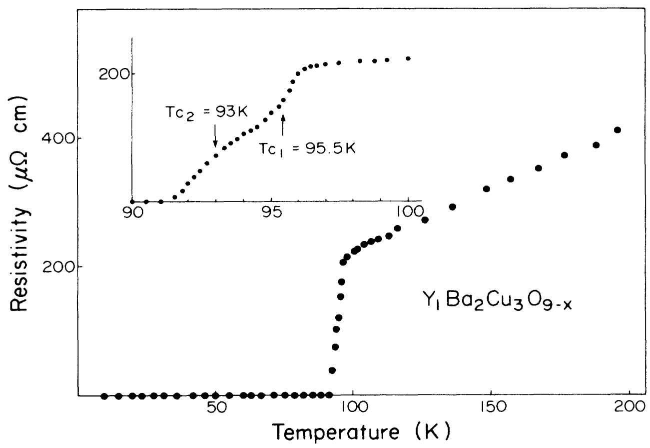

FIG. 2. Temperature dependence of resistivity. Inset shows two transition temperatures $T_{c1}=95.5$ K and $T_{c2}=93$ K.

composed of two different phases, each of which have $T_{c1}=95.5$ K and $T_{c2}=93$ K. It is not clear whether these two different T_c's are due to a yet-unidentified phase or are an intrinsic property of $Y_1Ba_2Cu_3O_{9-x}$, especially in the absence of any noticeable peak in the x-ray diffraction measurement. Above T_c, the sample shows metallic behavior with a linear temperature dependence in the resistivity. The linearity is $d\rho/dT=1.94\ \mu\Omega\,cm/K$. The resistivities at room temperature and at $T=98$ K just above T_c are $\rho(300)=520\ \mu\Omega\,cm$ and $\rho(98)=220\ \mu\Omega\,cm$, respectively. The sample, which was quench cooled to room temperature after the sintering process, in almost all cases showed semiconductorlike temperature dependence in the resistivity measurement, with the resulting T_c ranging from 50 to 70 K.

ac magnetic susceptibility measurements using an induction bridge were also made on the same sample in the temperature range 60 to 100 K. The onset temperature of diamagnetism is in good agreement with the resistance measurement as shown in Fig. 3. Separate ac susceptibility measurement from 60 down to 4.2 K did not show any noticeable structure. Although it is difficult to separate the contribution from shielding and the Meissner effect in the ac susceptibility measurement, a rough estimate by comparison with the signal size of standard bulk Pb indicates that the observed Meissner effect is about 50% of the complete diamagnetism. The magnitude of diamagnetism indicates that the bulk of the sample is in the superconducting phase.

In Fig. 4 we have plotted the result of the thermoelectric power measurement in the temperature range from 10 to 300 K on a sample which showed metallic behavior above $T_c=93$ K. In this measurement the thermoelectric power S is corrected for the contributions from the lead wire, and a temperature difference $\Delta T=1$ K was employed. The accuracy of our thermopower measurement is within $\pm 0.2\ \mu V/K$. Abrupt and complete disappearance of S below $T_c=92$ K within the experimental error again clearly indicates that the transition is of superconductive transition. The magnitude of S ($\sim\mu V/K$) above T_c indicates that Y-Ba-Cu-O is of a metallic nature, as expected from the resistivity measurement, while the negative sign of S indicates that Y-Ba-Cu-O is of n type. The most prominent feature of our thermopower measurement is the unusual shape of the "phonon-drag" effect[10] which rises discontinuously to $S=4\ \mu V/K$ at T_c and then decreases linearly in absolute magnitude as the temperature increases. The downturn of S above $T=270$ K is attributed to the electron diffusive contribution. Compared to the thermopower of $BaPb_{1-x}Bi_xO_3$, which shows a phonon-drag effect from $T=13$ to 50 K with the peak temperature at around 25 K,[11] $Y_1Ba_2Cu_3O_{9-x}$ shows an unusually strong effect over a wide temperature range from T_c to 270 K. The strong enhancement in the phonon-drag effect may indicate unusually strong electron-phonon coupling through, for example, high-frequency breathing-mode coupling witnessed in the structural distortion in this material. Detailed analysis of the thermopower results could lead to a better understanding of the nature of the superconducting mechanism of this material. Furthermore, if one takes the slope of S vs T near room temperature where the electron diffusion term begins to appear

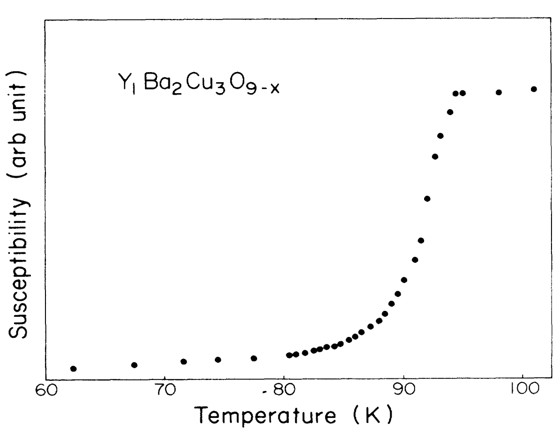

FIG. 3. ac magnetic susceptibility of $Y_1Ba_2Cu_3O_{9-x}$. Onset temperature is 93.5 K in good agreement with the resistivity measurement.

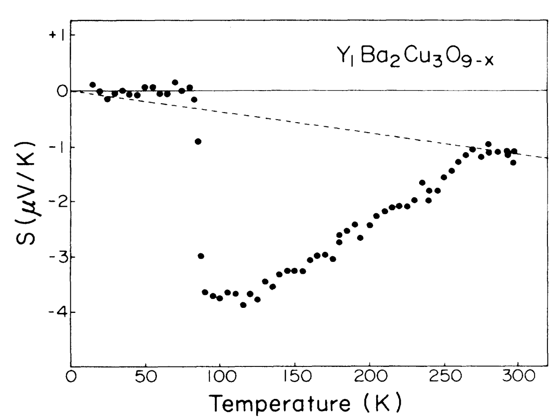

FIG. 4. Thermoelectric power of $Y_1Ba_2Cu_3O_{9-x}$ shows strongly enhanced "phonon-drag" effect.

(dashed line in Fig. 4), one can roughly estimate the upper limit of the density of states, $N(E_f)=0.3$ states/eV Cu atom, at the Fermi surface.

In summary, we have synthesized single-phase $Y_1Ba_2Cu_3O_{9-x}$ with $T_c=93$ K. X-ray measurement reveals that the $Y_1Ba_2Cu_3O_{9-x}$ phase has a slightly distorted perovskite structure. It appears from the resistivity measurement that there might be two different T_c's involved in this material. The strong enhancement and the unusual temperature dependence of the thermopower indicates that the superconductivity in this material may not be the ordinary phonon-mediated type.

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