Upper critical fields and high superconducting transition temperatures of $La_{1.85}Sr_{0.15}CuO_4$ and $La_{1.85}Ba_{0.15}CuO_4$

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The superconducting transition temperature T_c of $La_{1.85}Sr_{0.15}CuO_4$ is measured to be 34.7 K (midpoint) with a transition width (10–90%) of 2.6 K. The critical field slope at T_c is 2.13 T/K. Using the Werthamer, Helfand, and Hohenberg expression in the dirty limit we estimate the upper critical field $H_{c2}(0)$ to be at least 50 T for this system. The measured transition width broadens initially with increasing field to 4 K, then saturates at this value for fields above 2 T. The critical field slope for the lower T_c material $La_{1.85}Ba_{0.15}CuO_4$ is measured to be 1.78 T/K, which yields an $H_{c2}(0)$ of at least 36 T.

Recently a new class of superconductors has been discovered with the promise of unprecedented transition temperatures. Bednorz and Muller reported the onset of superconductivity in the LaBaCuO system[1] above 30 K; however, zero resistance was not achieved until temperatures near 10 K. Subsequently, Uchida *et al.* reported zero resistance at 23 K with onsets at 35 K for the system[2] $La_{1.85}Ba_{0.15}CuO_{4-y}$ where y indicates the presence of O vacancies. Recently, Jorgensen *et al.* report neutron diffraction measurements which assign the formula[3] $La_{1.85}Ba_{0.15}CuO_4$ to the superconducting phase. These samples also have broad superconducting transitions with onsets at 33 K and zero resistance at 19 K. The neutron diffraction results indicated a strain field involving significant displacement of near-neighbor oxygen atoms around the Ba defect and also a highly strained c axis of the unit cell when Ba is substituted for La. We believe this strain is responsible for the broad transitions reported for this compound.[2,3] The results of Jorgensen *et al.*[3] suggest that the role of Ba in this compound is to prevent the tetragonal I4/mmm structure from undergoing a Peierls $2K_f$ instability. We have therefore made a Sr-substituted sample with the same composition as the Ba-doped sample in order to avoid this c-axis strain (since the Sr ionic radius more closely matches that of La), and still provide the same electron transfer necessary to stabilize the tetragonal structure.

The samples have been prepared using a co-precipitation technique followed by pressing and sintering. In this technique the soluble nitrates of La, Cu, and Ba or Sr are mixed in solution in their correct proportions. After thorough mixing (usually $\gtrsim 30$ min with a magnetic stirrer) the materials are co-precipitated as insoluble oxycarbonates through the addition of sodium carbonate. The precipitate is filtered and washed until the pH of the rinse solution is neutral, then dried overnight in a 140 °C drying oven.

The co-precipitation technique, although time consuming, has the advantage of more uniform mixing than oxide powder techniques. This chemistry was chosen over the oxalate and citrate techniques described earlier[1,2] since, in those techniques, it is difficult to be sure of the stoichiometry of the final product because all of the Ba or Cu may not precipitate out of solution. In the carbonate technique, by carefully adjusting the pH of the solution to neutral prior to precipitation, all of the components come out of solution, and the stoichiometry is accurately known.

The dried oxycarbonate powder mixtures are then fired at 825 °C for 2 h to decompose the carbonates into oxides. The 2θ x-ray diffraction patterns clearly show the formation of the tetragonal phase even at this low temperature, indicating the high degree of intimate mixing achieved with this technique. The oxide powders are then pressed using a 3/8-in. die to approximately 60% of the theoretical density and sintered at 1100 °C in air for 4 h. The resulting pellets are generally about 80% of the theoretical density of 7.14 g/cc. Resistivity samples are cut from the pellets using a diamond wire saw.

Using a four-probe dc resistance measurement, with a sample current of 1 mA, we have measured the transition temperatures of both the Sr- and Ba-doped materials in fields to 6 T. Both samples have onset temperatures near 40 K; however, the Sr-doped sample reaches zero resistance above 30 K. The best Ba-doped sample has zero resistance at 23 K, while for other samples the values are as low as 19 K. In both systems the sample current was increased by two orders of magnitude without strongly influencing T_c. For sample currents of 50 mA and above, hysteresis effects indicate that sample heating occurs. This causes the large drop in T_c observed at higher currents (see inset). However, the zero resistance state below T_c is preserved even for the larger sample currents. This demonstrates that true zero resistance is being observed below T_c. In Fig. 1 we show the zero-field resistive transitions for both the Sr- and Ba-doped samples. The dramatic improvement in transition width for the Sr-doped sample should be noted. The bulk of this transition has a midpoint of 34.7 K with at $\Delta T_c = 2.6$ K (10–90% transition width). The width of the transition broadens to ~ 4 K in magnetic fields then saturates at this value above 2 T. We associate this improvement in transition width with the reduction of the c-axis strain in this compound, as compared to the Ba-doped compound, achieved by substituting with Sr. The small resistive foot at the bottom of the transition is sample dependent, and we believe, is due to small amounts of lower T_c material remaining in this sample.

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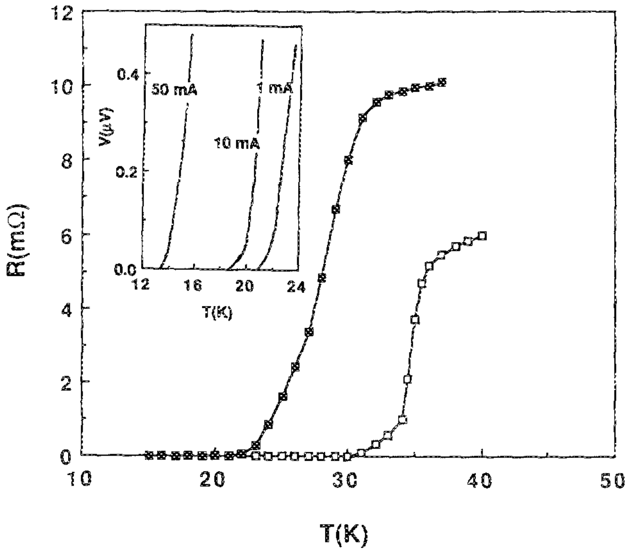

FIG. 1. Superconducting transition temperature in zero field as measured with a four-probe dc resistance for $La_{1.85}Ba_{0.15}CuO_4$ (■) and $La_{1.85}Sr_{0.15}CuO_4$ (□). The inset shows the effect of sample current on the $La_{1.85}Ba_{0.15}CuO_4$ sample.

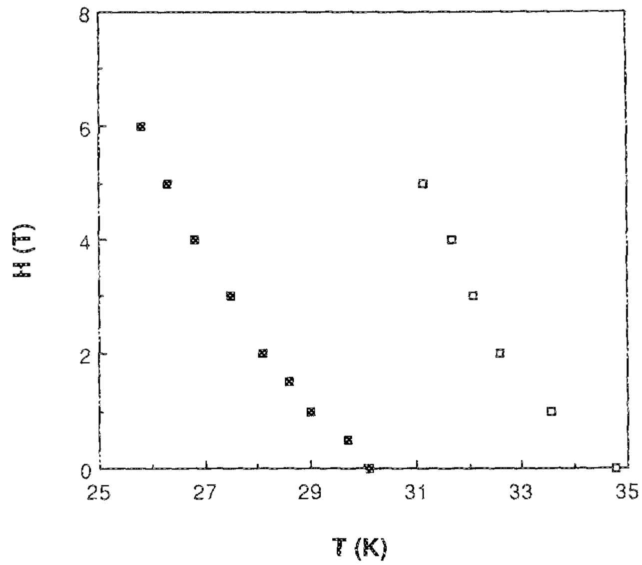

FIG. 2. Superconducting transition temperature (midpoints) vs magnetic field for $La_{1.85}Ba_{0.15}CuO_4$ (■) and $La_{1.85}Sr_{0.15}CuO_4$ (□).

Using transitions measured in fields up to 6 T we have determined the critical field slope near T_c. In Fig. 2 we show the critical field data for both the Sr- and Ba-doped samples. These data are determined using the midpoints of the resistive transitions. The critical field slopes of these data at T_c are 2.13 T/K and 1.78 T/K for the Sr- and Ba-doped samples, respectively. Using the Werthamer, Helfand, and Hohenberg (WHH) expression[4] in the dirty limit

$$H_{c2}(0) = 0.69 \frac{dH_{c2}}{dT}\bigg|_{T_c} T_c ,$$

we determine that $H_{c2}(0) \cong 50$ and 36 T for the Sr- and Ba-doped samples, respectively. Because of the limited amount of data, in field, for each sample these estimates of $H_{c2}(0)$ are approximate at best. However, for new materials such as these, we felt it important to demonstrate the potential for large upper critical fields in these materials for two reasons. Firstly, unpublished reports suggest[5] that the Ba-substituted materials do not have large upper critical fields. Moreover, a similar low electron density superconducting system, $BaPb_{1-x}Bi_xO_3$,[6] does not possess large upper critical fields. Secondly, there are remarkable technical possibilities suggested by such large H_{c2} values. Measurements in pulsed magnetic fields up to 45 T are in progress at the Francis Bitter National Magnet Laboratory and will be reported in a subsequent publication.

Superconducting transition temperatures of 35 K are measured for $La_{1.85}Sr_{0.15}CuO_4$ with onsets near 40 K. The transition widths are < 3 K due to a reduction of the c-axis strain by substituting with Sr instead of Ba. The critical field slopes at T_c have been measured to be 2.13 and 1.78 T/K, which yield $H_{c2}(0) \sim 50$ T and 36 T using the WHH expression for the Sr- and Ba-doped samples, respectively.

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[1] J. G. Bednorz and K. A. Muller, Z. Phys. B **64**, 189 (1986).
[2] S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. (in press).
[3] J. D. Jorgensen, D. G. Hinks, D. W. Capone, II, K. Zhang, H.-B. Schüttler, and M. B. Brodsky (unpublished).
[4] H. F. Werthamer, S. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 195 (1966).
[5] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang (unpublished).
[6] S. Foner (private communication).