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Single-phase 60-K bulk superconductor in annealed $Ba_2YCu_3O_{7-\delta}$ $(0.3 < \delta < 0.4)$ with correlated oxygen vacancies in the Cu-O chains

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Employing a gettered annealing technique, we have prepared homogeneous polycrystalline samples of oxygen-deficient $Ba_2YCu_3O_{7-\delta}$ for $0 \le \delta \le 0.7$. Measurements of resistive T_c, resistivity, magnetization, and lattice parameter indicate that a distinct bulk superconducting phase with a T_c of 60 K occurs in the range of $0.3 < \delta < 0.4$. This phase displays partial ordering of oxygen vacancies in the Cu-O chains as found by electron diffraction studies.

The 91-K bulk superconducting phase in the Ba-Y-Cu-O chemical system[1] has been identified as the perovskite-based $Ba_2YCu_3O_{7-\delta}$.[2-5] The compound exists over a range of oxygen concentration $0 \le \delta \le 1$ with its behavior changing from superconducting near $\delta = 0$, to semiconducting near $\delta = 1$.[6-12] The oxygen has been shown to be removed from between Cu(1) atoms in the chains,[12-14] and finally for $\delta = 1$ the Cu(1) atoms are isolated from each other (without intermediary oxygen atoms) in a linear O-Cu-O coordination characteristic of Cu^{1+}.

In this Rapid Communication we present the results of a study of the properties of polycrystalline $Ba_2YCu_3O_{7-\delta}$ prepared by a gettered annealing technique[15] which results in samples with uniform oxygen deficiency. The materials are considerably more homogeneous than those previously reported by quenching[16] or flow-gas techniques.[8] The possible existence of a superconducting phase near 55 K in reduced $Ba_2YCu_3O_{7-x}$ was first pointed out in ac susceptibility measurements on samples prepared in flowing gas which were a mixture of 91- and 55-K materials.[8] Powder x-ray diffraction indicates that the materials prepared by gettered annealing are single phase of orthorhombic symmetry over the entire range of nonstoichiometry studied. The sharp resistive and magnetic transitions have allowed us to determine that T_c is approximately constant near 90 K for $0 \le \delta \le 0.2$, then drops sharply to 60 K for $0.3 \le \delta \le 0.4$, and finally drops less sharply to ≈ 30 K at $\delta = 0.7$. The 60-K superconducting phase displays magnetic-flux exclusion equivalent to that of the 90-K phase. Taken in conjunction with room-temperature resistivities, which show a minimum near $\delta \sim \frac{1}{3}$, the results suggest that a short- or long-range ordered oxygen vacancy phase with a 60-K T_c exists near the composition $Ba_2YCu_3O_{7-1/3}$. This vacancy correlation is directly confirmed by electron diffraction studies. Thus, when 30%–40% of these specific oxygen sites are empty, and the vacancies are partially ordered, the superconducting transition drops by $\sim \frac{1}{3}$ from 90 to 60 K.

A master batch of $Ba_2YCu_3O_7$ was prepared from $BaCO_3$, Y_2O_3, and CuO by firing in Pt at 900 and 950 °C in air for three days with intermediate grindings. The powder was then pressed into pellets of weight $\frac{3}{4}-1$ g and fired suspended in Al_2O_3 boats for 16 h at 1000 °C in flowing O_2. The pellets were then annealed for 12 h at 500 °C in flowing O_2. The resulting pellets had the composition $Ba_2YCu_3O_{7.00}$. They were cut in half and sealed in evacuated quartz tubes 15 mm in diameter and 150 mm in length with a piece of degreased Zr foil of area approximately 2.5×2.5 cm^2. The tubes were then placed into furnaces at temperatures between 360 and 520 °C at 20–30 °C intervals for 48 h. Increasing amounts of O_2 were removed from the samples with increasing annealing temperature. The actual amount of oxygen removed is also dependent on the weight of the sample and the area of the Zr foil. The 48-h annealing time results in uniform oxygen distribution within the samples, and allows sufficient time for the possibility of defect ordering if it is operative. Samples were air quenched to room temperature.

Bars for resistivity measurements were cut from the centers of the annealed pellets, with approximate dimensions $2 \times 2 \times 7$ mm^3, and were measured in a four-probe configuration with indium contacts. Neighboring sections of each sample were cut out for magnetization measurement [SHE superconducting quantum interference device (SQUID) magnetometer 905] and oxygen analysis (TGA, Perkin Elmer). Powder x-ray diffraction patterns were recorded on a Rigaku diffractometer with Cu $K\alpha$ radiation, and the electron diffraction studies were done on a JEOL 2000 FX transmission electron microscope.

The results of the resistive measurements of T_c as a function of oxygen stoichiometry are shown in Fig. 1. The 10%–90% transition widths, indicated by the vertical bars, are quite narrow, indicating good sample homogeneity, except at the oxygen concentration where T_c is changing very quickly. The presence of a double plateau structure at 90 and 60 K is dramatic and unmistakable. This plateau is either not observed, or only suggested in materials prepared at higher temperatures by flowing-gas or quenching techniques. Also shown in the figure are the room-temperature resistivities ρ (see Table I also). Initially, ρ increases as expected from vacancy disorder, but there is a minimum in resistivity between $x = 6.6$ and $x = 6.7$, as would be expected for the occurrence of well (or better) ordered material. The resistivities then increase again for x values lower than 6.6. Although caution is advised in the interpretation of absolute values of resistivity in polycrystalline materials, the systematic vari-

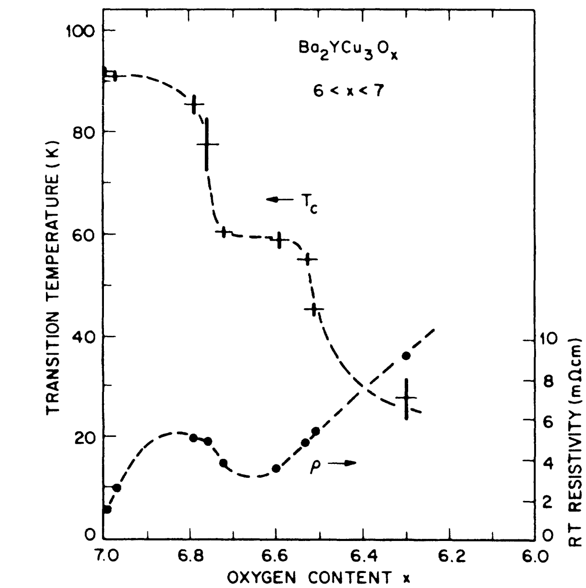

FIG. 1. Oxygen content dependence of the resistive superconducting transition temperature in $Ba_2YCu_3O_x$ for $6.3 \leq x \leq 7$. Vertical bars indicate the 10%–90% resistive transition width, with the midpoint marked with a cross. Also shown are the room-temperature resistivities.

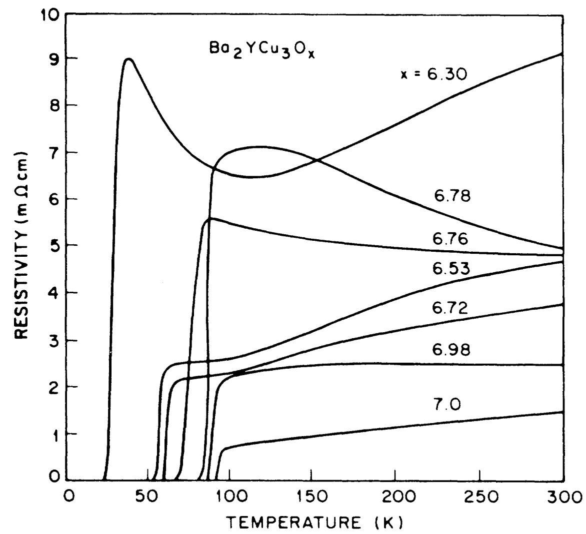

FIG. 2. Representative temperature-dependence resistivities for various amounts of oxygen deficiency in $Ba_2YCu_3O_x$. Note the nonmonotonic increase of the overall resistivity with decreasing oxygen concentration and the metallic character for $x = 6.72$ and 6.53.

ation with oxygen content appears to be highly significant and also reflects the high degree of control in the material preparation process. Resistivity versus temperature curves for various values of oxygen concentration are presented in Fig. 2. Noteworthy is the rapid overall initial increase of ρ when oxygen vacancies are induced. When δ is near $\frac{1}{3}$ $(x \sim 6\frac{2}{3})$, however, this trend is reversed and $\rho(T)$ has a metallic characteristic, reminiscent of the "saturation" behavior of ρ found in many intermetallic compounds. This is the main evidence for a (partially) ordered phase in the range of $x \simeq 6.6$ to 6.7.

Representative magnetization data are shown in Fig. 3 for samples cooled in a magnetic field of 13 Oe. The diamagnetic signal is normalized to the one expected for the same solid volume and full diamagnetism. Within the error in estimating the volume of the samples, the amount of flux exclusion is equivalent for the 90- and 60-K T_c material, indicating that the 60-K material is also a good bulk superconductor. This is confirmed by Meissner effect data. We also note the sharpness of the transition for this sample and the significant broadening for $x = 6.76$. A reduced, but still large, normalized diamagnetism is measured for other samples and reflects either a reduced volume fraction of superconducting material or stronger flux trapping.

Although the data presented in Fig. 1 are consisted with the existence of two "single-phase" regions with T_c's near 90 and 60 K with bounding "two-phase" regions where T_c changes with composition, the powder x-ray diffraction data indicate that the compounds are single phase with orthorhombic symmetry over the whole composition range studied. The variation of lattice parameters with stoichiometry is shown in Fig. 4. We have drawn a

TABLE I. Orthorhombic cell parameters and resistivities of $Ba_2YCu_3O_x$ at room temperature.

x	a_0(Å)	b_0(Å)	c_0(Å)	δ (mΩ cm)
7.0	3.822(1)	3.891(1)	11.677(2)	1–1.5
6.78	3.827(2)	3.895(2)	11.722(7)	5
6.76	3.830(2)	3.898(2)	11.728(6)	4.9
6.72	3.835(4)	3.890(4)	11.716(11)	3.8
6.60	3.831(2)	3.889(2)	11.736(6)	3.5
6.53	3.838(2)	3.887(2)	11.747(6)	4.7
6.51	3.845(3)	3.887(3)	11.768(8)	5.4
6.30	3.851(5)	3.883(5)	11.789(16)	9.2

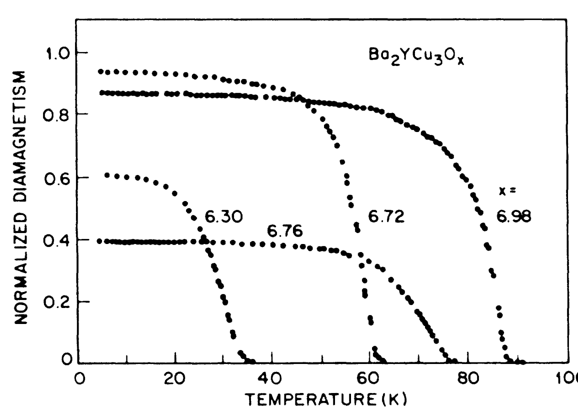

FIG. 3. Magnetization for $Ba_2YCu_3O_x$ samples cooled in a magnetic field of 13 Oe. The diamagnetic signal is normalized to the value expected for full diamagnetism.

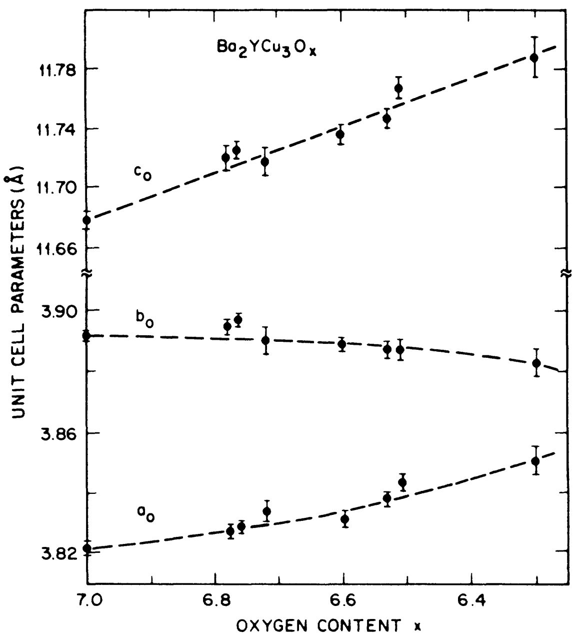

FIG. 4. Oxygen content dependence of the crystallographic cell parameters for $Ba_2YCu_3O_x$, measured at room temperature after annealing for 48 h at elevated temperatures.

smooth variation of all parameters with composition, although more detailed measurements might reveal the presence of different composition or cell parameter regions. The powder x-ray diffraction data describe the average structure (substructure) and are insensitive to either short-range oxygen or vacancy ordering, which would result in diffuse scattering, or very weak superstructure diffraction peaks ($< 1\%$ of I_{max}), which would arise from long-range ordering.

In the search for vacancy ordering we performed electron diffraction studies on $x = 6.72$ samples and indeed found diffuse scattering. In diffraction from a single domain, additional intensity is seen in the a^*b^* plane and is located halfway between Bragg reflection along b^* in the form of narrow streaks elongated in the b^* direction. This suggests vacancy ordering and is very similar to one of the ordering types reported in Ref. 17 for oxygen-deficient $Ba_2YCu_3O_{7-\delta}$. Further studies will concentrate on identifying the actual three-dimensional arrangement and address the question of how a variable macroscopic vacancy concentration is accommodated microscopically. We note in this context that the range of x where the 60-K phase is observed encompasses several simple whole ratios of occupied and empty oxygen sites in the chains, such as, e.g., $\frac{5}{8}$, $\frac{2}{3}$, and $\frac{3}{4}$.

It has generally been reported that $Ba_2YCu_3O_x$ changes from orthorhombic to tetragonal symmetry for x less than 6.6 (see, for instance, Ref. 6). However, those data have either been obtained at elevated temperatures, or for samples quenched from higher temperatures than those employed in this long-term annealing study. We believe that both the extension of the orthorhombic symmetry to beyond $x = 6.3$ and the observation of a distinct 60-K superconducting phase are dependent upon the thermal conditions employed to obtain the oxygen stoichiometry. Samples prepared at higher temperatures are not likely to display the features reported here.

By employing a gettered annealing technique, we have studied the oxygen dependence of the physical properties in $Ba_2YCu_3O_x$ for samples prepared below 520 °C. The average structure of the materials produced is orthorhombic over the whole range of compositions studied ($6.3 \leq x \leq 7.0$). The existence of a distinct bulk superconducting phase with a T_c of ~ 60 K for x between 6.6 and 6.7 is revealed, in which the oxygen atoms and vacancies in the Cu-O chains are partially ordered. We conclude that the spatial arrangement of the oxygen atoms, and not only their average concentration, determines the superconducting transition temperature.

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[1]M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[2]R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. M. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[3]T. Siegrist, S. Sunshine, D. W. Murphy, R. J. Cava, and S. M. Zahurak, Phys. Rev. B **35**, 7137 (1987).

[4]R. P. Grant, R. B. Beyers, E. M. Engler, G. Lim, S. S. P. Parkin, M. L. Ramirez, V. Y. Lee, J. E. Vazquez, and R. J. Savoy, Phys. Rev. B **35**, 7242 (1987).

[5]Y. LePage, W. R. McKinnon, J. M. Tarascon, L. H. Greene, G. W. Hull, and D. M. Huang, Phys. Rev. B **35**, 7245 (1987).

[6]P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, and D. W. Murphy, Mater. Res. Bull. **22**, 995 (1987).

[7]A. Santoro, S. Miraglia, F. Beech, S. A. Sunshine, D. W. Murphy, L. F. Schneemeyer, and J. V. Waszczak, Mater. Res. Bull. **22**, 1007 (1987).

[8]J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, B. G. Bagley, E. M. Vogel, and Y. Le Page, in Proceedings of the 1987 Spring Materials Research Society Meeting, edited by D. V. Gubser and M. Schluter (unpublished).

[9]I. K. Schuller, D. G. Hinks, M. A. Beno, D. W. Capone II, L. Souderholm, J. P. Locquet, Y. Bruynseraede, C. U. Segre, and K. Zhang, Solid State Commun. **66**, 385 (1987).

[10]J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki, and A. P. Paulikas, this issue, Phys. Rev. B **36**, 5731 (1987).

[11]M. P. A. Viegers, D. M. de Leew, C. H. A. Mutsaers, H. C. A. Smoorenburg, J. H. T. Hengst, J. W. C. de Vries, and P. C. Zalm (unpublished).

[12]R. Beyers, G. Lim, E. M. Engler, R. J. Savoy, T. M. Shaw, T. R. Dinger, W. T. Gallagher, and R. L. Sandstrom, Appl.

Phys. Lett. **50**, 1918 (1987).
[13]F. Beech, S. Miraglia, A. Santoro, and R. S. Roth, Phys. Rev. B **36**, 8778 (1987).
[14]A. W. Hewat, J. J. Capponi, C. Chaillout, M. Marezio, and E. A. Hewat, Solid State Commun. (to be published).
[15]C. Chaillout and J. P. Remeika, Solid State Commun. **56**, 833 (1985).
[16]H. Sawada, T. Iwazumi, Y. Saito, Y. Abe, M. Ikeda, and R. Yoshizaki, Jpn. J. Appl. Phys. (to be published).
[17]C. Chaillout, M. A. Alario-Franco, J. J. Capponi, J. Chenavas, and M. Marezio (unpublished).