LETTERS TO THE EDITOR

Influence of Ca on the Superconductivity of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$

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Substitution of Ca for Y does not increase the maximum oxidation state of the $(CuO_{3-\delta})^{(3-x)-}$ layers of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ ($0 \leq x < 0.3$); as x increases so does the minimum value of δ obtained by annealing in an oxygen atmosphere at temperatures 350–450°C. The superconducting transition temperature T_c decreases from 87 K for $x = 0$ to about 66 K for $x = 0.3$ despite a nearly constant total formal oxidation state for the copper. A broad transition for the $x = 0.2$ and 0.3 samples suggests a tendency to segregate into two phases of different oxygen content having different values of T_c. The normal state remains metallic above T_c. The lattice parameter variation with x has been monitored for samples air-quenched from 450°C. © 1988 Academic Press, Inc.

Introduction

The high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ exhibits a remarkable dependence on the concentration and order of its oxygen. Thermogravimetric analysis (TGA) has shown (1) that the intercalation/disintercalation of oxygen is rapid at temperatures $T \geq 400°C$ if the sample is prepared in air in the interval $900°C \leq T \leq 950°C$ and cooled in air. This procedure allows the sample to establish an orthorhombic structure below an order–disorder transition temperature (2) near 750°C where $(7 - \delta) < 6.5$. Under these conditions, the maximum oxygen concentration is obtained by annealing in oxygen at 350–450°C and furnace cooling (1–3). This procedure yields a maximum (7

$- \delta) \approx 6.94$, and it gives the highest T_c with the sharpest transition (3).

The intergrowth structure has no oxygen in the Y^{3+}-ion planes, which creates a strong internal electric field parallel to the c-axis between these planes and the oxygen-intercalation planes; the situation is analogous to that identified in the magnetoplumbite structure (4). As a result, the oxidation/reduction reactions associated with oxygen intercalation/disintercalation tend to be constrained to the $(CuO_{3-\delta})^{3-}$ layers between Ba^{2+}-ion planes. These copper are designated Cu(1). The copper in planes adjacent to the Y^{3+}-ion layers are labeled Cu(2); we assume for simplicity that these remain divalent for all oxygen concentrations.

The purpose of the experiments reported here was to inquire whether, by substituting Ca for Y, it would be possible to increase

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the maximum value of $(7 - \delta)$ obtained by annealing in oxygen in the range $350°C < T < 450°C$. It proved impossible to accomplish this goal; it was found instead that there is an intrinsic limit to the oxidation state of the $(CuO_{3-\delta})^{(3-x)-}$ layer in this structure. The oxidation state of the layer remains $(CuO_{3-\delta_0-0.5x})^{(3-x)-}$ for all x, where δ_0 is the equilibrium value for $x = 0$ at a particular temperature and partial pressure of oxygen.

Experimental

The compositions $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ ($0 \le x \le 0.3$) were prepared by firing required quantities of Y_2O_3, $BaCO_3$, CuO, and $Ca CO_3$ at 920°C for about 36 hr with an intermittent grinding. The formed product was cooled to 450°C in the furnace over 3 to 4 hr; it was then annealed at that temperature for 10 hr and air-quenched. In order to obtain maximum oxygen content, the samples were then annealed in the range 400–450°C in pure oxygen for 15 hr and cooled slowly in the furnace, stopping at 350°C for 10 hr before continuing to room temperature.

The products were characterized by powder X-ray diffraction with a Philips diffractometer fitted with a diffracted-beam monochromator and $CuK\alpha$ radiation. Lattice parameters were determined with NaCl as the internal standard.

The average formal oxidation state of copper, and therefore the total oxygen content of the sample, was determined by iodometric titration as previously reported (1). Oxygen analysis at temperature was then obtained by TGA. The TGAs were carried out in a Perkin–Elmer Series 7 thermal-analysis system in oxygen and nitrogen atmospheres.

Superconducting transition temperatures were determined by measuring the resistance of sintered pellets by the four-probe technique. The pellets were annealed in oxygen at about 400–450°C for 15 hr and then at 350°C for 10 hr before being slowly cooled in the furnace prior to the resistance measurement. The value of T_c was taken to be the midpoint of the sharp drop in the resistance.

Results and Discussion

X-ray powder diffraction on samples prepared to give a maximum $(7 - \delta)$ indicated that the $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ samples having $0 \le x < 0.3$ were all single-phase and had the same orthorhombic structure; the sample with $x = 0.3$ showed weak reflections due to the impurity phase $BaCuO_2$, which indicates that it is beyond the limit of the solid–solubility range.

The variations with x of lattice parameters and unit-cell volume, Fig. 1 and Table I, show an increase in the basal-plane area
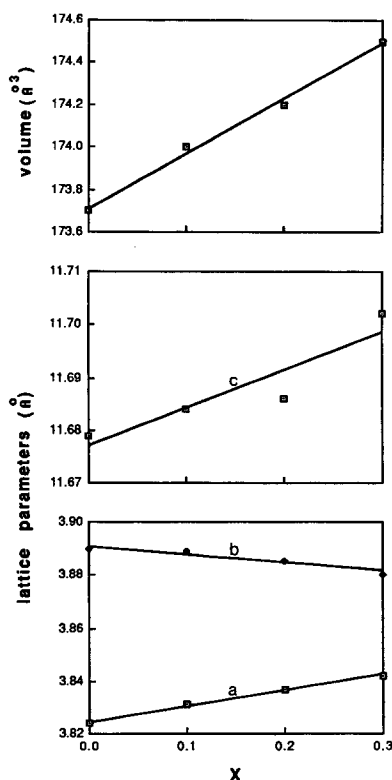

FIG. 1. Variation of lattice parameters with x for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ air-quenched from 450°C.

TABLE I

ANALYTICAL RESULTS AND LATTICE PARAMETERS OF $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$

	Formal valence of Cu(1)		$7 - \delta$		Lattice parameter (Å)^c			Volume (Å^3)
x	Air^a	Oxygen^b	Air^a	Oxygen^b	a	b	c	
0.0	2.70	2.88	6.85	6.94	3.824(1)	3.890(1)	11.679(2)	173.7
0.1	2.68	2.84	6.79	6.87	3.831(1)	3.889(1)	11.684(3)	174.0
0.2	2.68	2.84	6.74	6.82	3.837(2)	3.885(2)	11.686(5)	174.2
0.3^d	2.60	2.72	6.65	6.71	3.842(2)	3.880(2)	11.702(5)	174.5

^{a} Air-quenched from 450°C.
^{b} Oxygen-annealed at 350–450°C as given in the text.
^{c} For samples air-quenched from 450°C.
^{d} This sample contained some $BaCuO_2$ impurity.

and unit-cell volume to be expected for substitution of the larger Ca^{2+} ion for Y^{3+}. On the other hand, the b-axis shows a contraction with increasing x, indicating loss of b-site oxygen associated with a smaller value of $(7 - \delta)$. The substitution of Ca for Y is established by these variations in lattice parameter with x and, more clearly, by the decreasing separation of the following pairs in the X-ray diffraction pattern: (i) 013 and 103 + 110, (ii) 006 + 020 and 200, and (iii) 116 + 123 and 213.

The average formal valence state of Cu(1)—obtained by assuming all Cu(2) and oxygen are divalent—and the total oxygen content $(7 - \delta)$ are given in Table I as a function of x for samples as initially annealed at 450°C in air and after subsequently annealing in oxygen. The remarkable finding is that the average formal oxidation state of copper is essentially independent of x in the single-phase samples. This means that the oxygen concentration $(7 - \delta)$ obtained by these two different treatments decreases as $-0.5x$, which indicates that for a given partial pressure of oxygen and temperature the rapid oxidation process of the $(CuO_{3-\delta_0-0.5x})^{(3-x)-}$ layers proceeds to a fixed limit that is independent of x (provided there is no peroxide formation (5)).
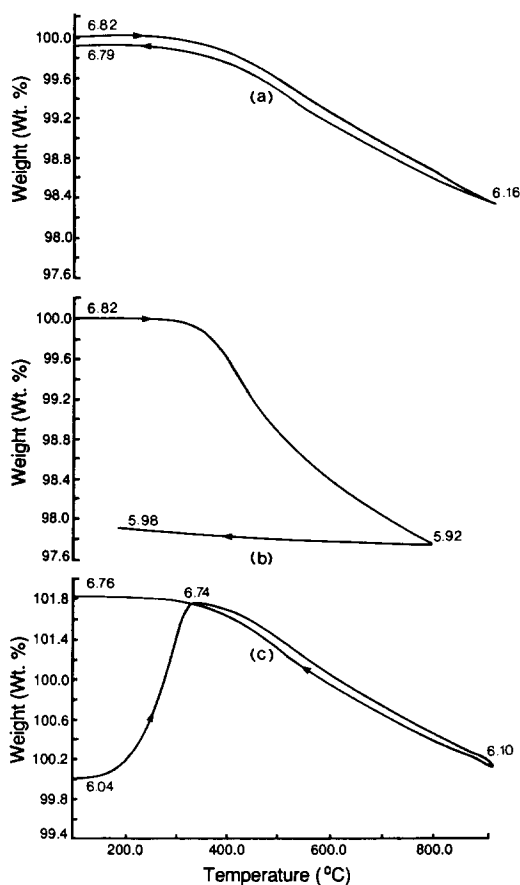

FIG. 2. TGA curves for starting composition $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.82}$ in (a) O_2 and (b) N_2 atmospheres and (c) for starting composition $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.04}$ in O_2. The numbers refer to oxygen content.
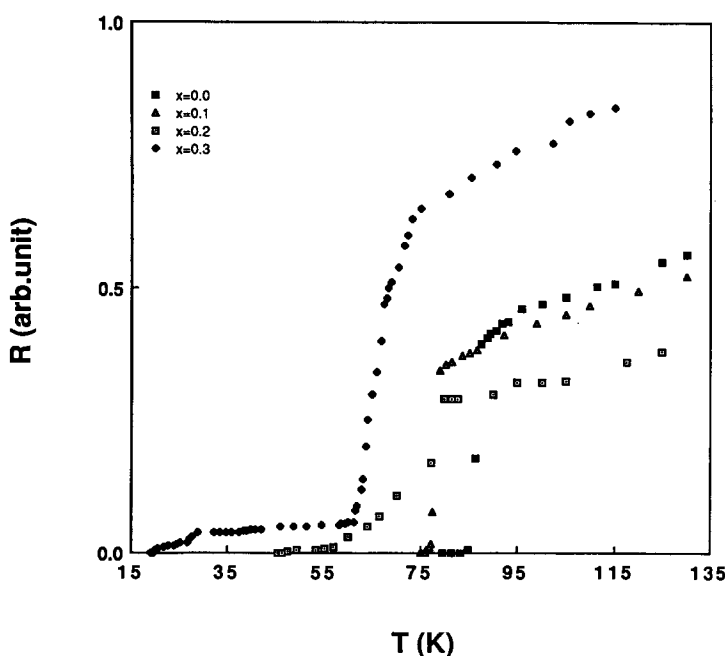
FIG. 3. Resistance versus temperature for $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ oxygen-annealed at 350–450°C.

The TGA curve for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.82}$ heated and cooled in an oxygen atmosphere at 1°C/min is shown in Fig. 2a. Heating to 905°C produced a composition $(7 - \delta) = 6.16$; during cooling oxygen is reversibly reintercalated to yield a composition $(7 - \delta) = 6.79$. Figure 2b shows the corresponding TGA curve for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.82}$ heated in N_2 atmosphere at 2°C/min and cooled in N_2 atmosphere at 20°C/min. The sample starts losing oxygen near 350°C and reaches a composition $(7 - \delta) = 5.92$ at 790°C. A slight up-take of oxygen occurs on cooling in nitrogen at 20°C/min; it appears to be due to O_2 contamination of the N_2 used. An X-ray diffraction pattern of the $(7 - \delta) = 5.98$ end product gave a tetragonal structure similar to that of $YBa_2Cu_3O_6$. Any removal of oxygen below O_6 would make the coordination number of copper in the $(Cu O_{3-\delta})^{(3-x)-}$ layer less than two unless some O–Cu–O units rotated 90°; alternatively, oxygen vacancies would have to be created in the CuO_2 layers.

A sample of composition $Y_{0.8}Ca_{0.2}Ba_2Cu_3 O_{6.04}$, obtained by heating in nitrogen at 750°C in a furnace followed by quenching, was subjected to TGA in an oxygen atmosphere (Fig. 2c). Rapid uptake of oxygen starts above 180°C and reaches an oxygen content of $(7 - \delta) = 6.74$ at about 350°C; it loses oxygen thereafter with increasing temperature, reaching a composition of $(7 - \delta) = 6.10$ at 905°C. Cooling in oxygen at 1°C/min produced a composition of $(7 - \delta) \simeq 6.76$. These experiments illustrate the reversibility of the oxygen intercalation also in the Ca-substituted compounds.

As can be seen in Fig. 3, the superconducting transition temperature decreases from 87 K for $x = 0$ to 78 K for $x = 0.1$; the transitions in the $x = 0.2$ and 0.3 samples $(T_c = 73$ and 66 K) are broad. Broadening of the transition for samples with $6.71 \leq (7 - \delta) \leq 6.82$ is consistent with a heterogeneous δ in a solid-solution range about a $(7 - \delta) = 6.75$ phase in which T_c varies rapidly with δ. For $x = 0$, a plateau in T_c vs x at $T_c \approx 60$ K

has been observed (6); it has been interpreted (7) to reflect a two-phase region between ordered phases at $(7 - \delta) = 6.5$ and 6.75. The decrease of T_c with increasing x reflects the smaller oxygen concentration at higher values of x for the same oxidation state of the $(CuO_{3-\delta})^{(3-x)-}$ layer.

For a fixed hole concentration $[h] \approx 1.9$ in the overlapping Cu(1)–3d and O–2p bands (calculated on the assumption that the Cu(2)–atom formal valence is fixed at Cu^{2+}), the measured variation $(\partial T_c/\partial(0.5x))_{[h]=1.9} = (\partial T_c/\partial[V_O])_{[h]=1.9} \approx -180$ K reflects the change in T_c with respect to the oxygen-vacancy concentration $[V_O]$ in the b-axis chains.

Acknowledgments

References

1. A. MANTHIRAM, J. S. SWINNEA, Z. T. SUI, H. STEINFINK, AND J. B. GOODENOUGH, J. Amer. Chem. Soc. 109, 6667 (1987).
2. R. KANNO, Y. TAKEDA, M. HASEQAWA, O. YAMAMOTE, M. TAKANO, Y. IKEDA, AND Y. BANDO, Mater. Res. Bull. 22, 1525 (1987).
3. J. M. TARASCON, W. R. McKINNON, L. H. GREENE, G. W. HULL, B. G. BAGLEY, E. M. VOGEL, AND Y. LEPAGE, "Proceedings of the Symposium on High Temperature Superconductors with T_c over 30 K, "Materials Research Society (1987).
4. J. FONTCUBERTA, X. OBRADORS, AND J. B. GOODENOUGH, J. Phys. C. 20, 441 (1987).
5. A. MANTHIRAM AND J. B. GOODENOUGH, Nature (London) 329, 701 (1987).
6. R. J. CAVA, B. BATLOGG, C. H. CHEN, E. A. RIETMAN, S. M. ZAHURAK, AND D. WERDER, Nature (London) 329, 423 (1987).
7. J. B. GOODENOUGH, J. Mat. Education, in press.