PHYSICAL REVIEW B VOLUME 44, NUMBER 5 1 AUGUST 1991-I

Control of the hole concentration in the $YBa_2Cu_3O_{6+z}$-type superconductors $(Yb,Ca)(Ba,Sr)_2Cu_3O_{6+z}$ with low and high Ca contents

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(Received 15 January 1991)

$(Yb_{1-x}Ca_x)$ $(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ $(0 \leq x \leq 0.4)$ solid solutions of the $YBa_2Cu_3O_{6+z}$ ("1:2:3") -type structure were successfully synthesized. The solid-solution samples were characterized with respect to the oxygen content, crystal structure, and superconducting properties. The "fully oxygenated" samples with $z \sim 0.8$ were prepared employing postannealing at high oxygen partial pressure atmosphere $[P(O_2)=400$ atm]. The samples had orthorhombic unit cells and showed bulk superconductivity. The superconducting transition temperatures (T_c's) ranged from 80 to 32 K, depending on the Ca content. Samples with $x=0.1$ and 0.3, and various oxygen contents ($0.36 \leq z \leq 0.89$ for $x=0.1$ and $0.10 \leq z \leq 0.78$ for $x=0.3$) were prepared by employing quenching and annealing techniques. For $(Yb_{0.7}Ca_{0.3})$ $(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$, as the oxygen content z decreased, T_c increased from 40 K first, then peaked at 82 K at $z=0.56$, and decreased down to 48 K at $z=0.10$. The relationship between T_c and the hole concentration in the CuO_2 sheet, p_{sheet}, was obtained. T_c was maximum at $p_{\text{sheet}}=0.18$ for both samples with $x=0.1$ and 0.3.

I. INTRODUCTION

The importance of the hole concentration in copper-oxide superconductors is widely recognized.[1] A number of studies concerning the relationship between the hole concentration (p) and the superconducting transition temperature (T_c) have been reported.[2] In the $La_{2-x}Sr_xCuO_4$ system, as the Sr content x, and therefore p, increases, T_c increases first to have a maximum and then becomes zero for $x \geq 0.26$.[3]

In $YBa_2Cu_3O_{6+z}$ (1:2:3), a tetragonal-orthorhombic structural phase transition and a stepwise increase in T_c are observed as the oxygen content increases, i.e., $6+z$.[4] $YBa_2Cu_3O_{6+z}$ consists of two kinds of oxygen-deficient perovskite blocks, i.e., the Y-CuO_2-BaO block with a fixed oxygen content and the BaO-CuO_z-BaO block with variable oxygen content.[5] The structural phase transition can be explained by a preferential ordering of oxygen in the CuO_z plane.[6] T_c for the $YBa_2Cu_3O_{6+z}$ system reaches a maximum plateau around $z \sim 1.0$.[2] Some attempts to demonstrate the decrease in T_c with increasing hole concentration was made for the $(Y_{1-x}Ca_x)Ba_2Cu_3O_{6+z}$ system.[7,8] However, the minimum T_c obtained was as high as 80 K because the solubility of Ca for the Y site in this system is low, being limited to $x=0.2$.[8]

A preliminary investigation was carried out to obtain the optimum composition in $(R_{1-x}Ca_x)(Ba_{1-y}Sr_y)_2Cu_3O_{6+z}$ (R being a rare-earth element) system with the high Ca content x. It was concluded that the highest Ca content, $x=0.4$, was obtained at $y=0.2$ when $R=$Yb. Therefore, the $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ system was chosen for studying the 1:2:3 superconductors with high hole concentrations. As was found in $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$, the superconducting transition temperatures linearly decreased with increasing Ca content when post annealed at $P(O_2)=400$ atm. The minimum T_c of 32 K was obtained for $(Yb_{0.6}Ca_{0.4})(Ba,Sr)_2Cu_3O_{6.71}$.

II. EXPERIMENT

The $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ samples with $x=0.0$, 0.1, 0.2, 0.3, and 0.4 were prepared by a solid-state reaction method. High-purity powders of Yb_2O_3, $CaCO_3$, $BaCO_3$, $SrCO_3$, and CuO were used as starting materials. Appropriate amounts of powders were mixed, calcined, and compacted. The bars were sintered at 850 °C for 20 h in a mixed gas of 99% N_2 and 1% O_2. The "fully oxygenated" samples 1–5 were obtained by post annealing at $P(O_2)=400$ atm and at 600 °C for 3 h and then at 400 °C for 3 h. The post annealing was made by using a hot isostatic pressing (HIP) technique.[9]

The $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ samples with lower oxygen contents (samples 6–10 for $x=0.1$ and samples 11–14 for $x=0.3$) were prepared employing quenching and annealing techniques. Some of the samples were re-heat-treated at 300 °C or 500 °C for 3 h in air and then quickly cooled into liquid nitrogen. The quenched sample was post annealed at about 450 °C for 100 h in an evacuated silica tube to obtain a homogeneous distribution of oxygen throughout the sample. Other quenched samples were reduced further using Ti_2O_3 as the reducing agent at about 500 °C for 100 h.

The lattice constants were determined by powder x-ray diffraction using Cu$K\alpha$ radiation. The average valence of copper was determined by a Coulometric titration technique.[10] A hydrochloric acid solution (1 N HCl) was used for the solvent. The 1 N HCl solution was free from dissolved oxygen and titrations were carried out in oxygen-free N_2 gas flow. In this technique, the concentration of a Cu^+ ion in the CuCl solution was previously determined by a blank titration. Then Cu^{3+} ions in the sample solutions reacted with Cu^+ ions (CuCl) and the excess of Cu^+ ions was titrated by an anodic oxidation as follows:

$$Cu^{3+} + Cu^{+} \rightarrow 2Cu^{2+} \ ,$$

$$Cu^{+}(\text{excess}) \rightarrow Cu^{2+} + e^{-} : \text{Coulometry} \ .$$

The oxygen content was calculated from the determined average Cu valence: the valences of the ions such as Yb, Ca, Ba, and Sr were considered to be constants, i.e., Yb^{3+}, Ca^{2+}, Ba^{2+}, and Sr^{2+}, respectively. This Coulometric titration technique allowed the determination of oxygen content to an accuracy of 0.02 per formula unit.[10]

Electrical resistivity measurements were carried out using a conventional dc four-probe method and the dc magnetic susceptibility measurements using a SQUID magnetometer (quantum design, model MPMS). The measurements were performed by decreasing temperature with a constant magnetic field of 10 Oe. Superconducting transition temperatures (T_c^{mag}'s) were determined from the temperature dependences of the dc magnetic susceptibility. T_c^{mag} was the highest temperature at which the sample showed a negative magnetic susceptibility.

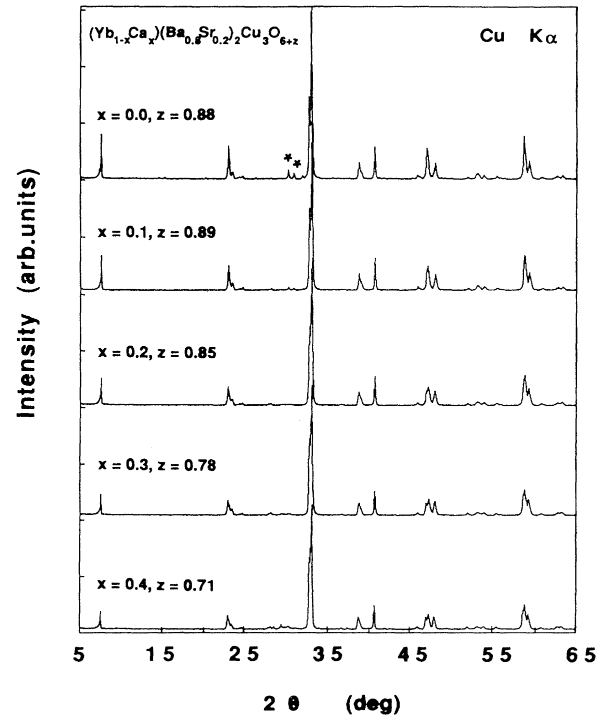

FIG. 1. X-ray powder diffraction patterns for $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ samples which were prepared by postannealing at $P(O_2)=400$ atm.

III. RESULTS

A. $(Yb,Ca)(Ba,Sr)_2Cu_3O_{6+z}$ with $z \sim 0.8$

Figure 1 shows the x-ray powder diffraction patterns for the $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ samples which were post annealed at $P(O_2)=400$ atm (samples 1–5). The peaks in the pattern are indexed for an orthorhombic unit cell with the lattice constants $a=3.79$ Å, $b=3.86$ Å, and $c=11.6$ Å. The crystal structures of these samples were of the orthorhombic $YBa_2Cu_3O_{6+z}$ type. The determined lattice constants for samples 1–5 are summarized in Table I. The lengths of the a and c axes slightly increased and that of the b axis decreased with increasing Ca content. The figure shows that the sample with $x=0.1$, 0.2, 0.3, and 0.4 (samples 2–5) were single phases and the samples with $x=0.0$ (sample 1) contained Yb_2BaCuO_5 as a minor impurity phase but the amount was estimated to be less than 5%. Therefore, we determined the oxygen content in the sample, disregarding the impurity phase.

The oxygen contents, $6+z$, of the samples are also summarized in Table I and they are plotted against the Ca content, x, in Fig. 2. This figure shows that the oxygen content monotonically decreases from 6.88 for the sample with $x=0.0$ to 6.71 for the sample with $x=0.4$, as x increases. It was not straightforward to obtain samples with high Ca contents and high oxygen contents.

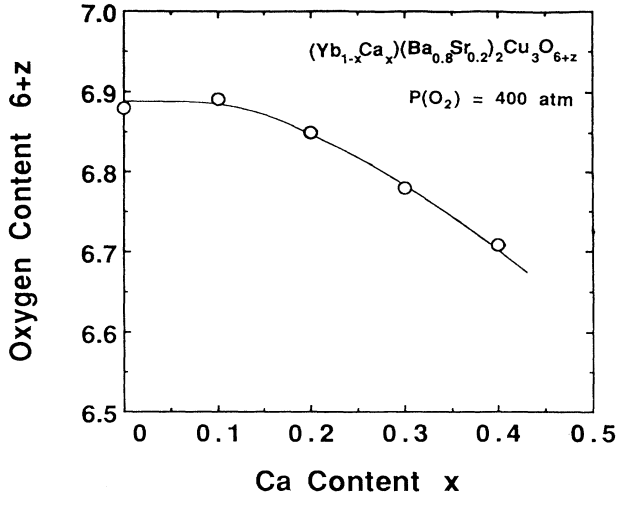

FIG. 2. The relation of oxygen contents, $6+z$, and the Ca content, x, for $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ samples which were prepared by postannealing at $P(O_2)=400$ atm.

TABLE I. Compositions, lattice constants, and superconducting properties of $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$. (Numbers in parentheses indicate standard deviations.)

Sample number	Composition x	z	Lattice constants a (Å)	b (Å)	c (Å)	T_c^{mag} (K)	χ at 10 K (10^{-3} emu/g Oe)
1	0.0	0.88	3.789(1)	3.866(1)	11.598(1)	80	4.7
2	0.1	0.89	3.789(1)	3.859(1)	11.600(1)	68	6.9
3	0.2	0.85	3.794(1)	3.854(1)	11.607(1)	48	5.8
4	0.3	0.78	3.794(1)	3.851(1)	11.622(1)	40	2.2
5	0.4	0.71	3.797(1)	3.851(1)	11.624(1)	32	2.4
6	0.1	0.86	3.790(1)	3.859(1)	11.603(1)	72	4.6
7	0.1	0.84	3.791(1)	3.859(1)	11.600(1)	76	6.4
8	0.1	0.69	3.800(1)	3.858(1)	11.611(1)	77	3.7
9	0.1	0.61	3.822(1)		11.686(1)	76	3.7
10	0.1	0.36	3.821(1)		11.745(1)	48	2.3
11	0.3	0.73	3.797(1)	3.856(1)	11.593(1)	68	4.3
12	0.3	0.56	3.830(1)		11.677(1)	82	4.3
13	0.3	0.43	3.822(1)		11.708(1)	64	3.3
14	0.3	0.10	3.817(1)		11.750(1)	48	1.4

The maximum average valence of the Cu ion obtained was 2.30 (for the sample with $x = 0.2$ and $z = 0.85$).

All of the samples 1–5 showed a metallic temperature dependence of resistivity and exhibited bulk superconductivity with sharp superconducting transitions. Figure 3 shows the temperature dependences of the dc magnetic susceptibility. The magnetically determined superconducting transition temperatures (T_c^{mag}'s) were 80 K for $x = 0.0$, 68 K for $x = 0.1$, 48 K for $x = 0.3$, and 32 K for $x = 0.4$. These values for T_c^{mag} were in good agreement with T_c's electrically determined. Thus, for the first time, we demonstrated a decrease in T_c for the $YBa_2Cu_3O_{6+z}$ superconductors as the hole concentration increased.

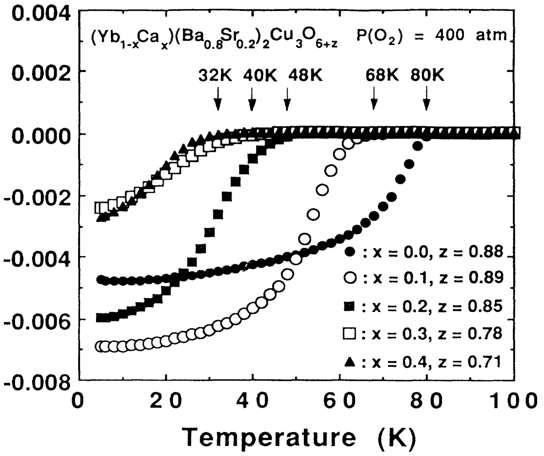

FIG. 3. Temperature dependence of the dc magnetic susceptibility for $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ samples which were prepared by postannealing at $P(O_2) = 400$ atm.

B. Control of oxygen content in $(Yb,Ca)(Ba,Sr)_2Cu_3O_{6+z}$

Figure 4 shows the x-ray powder diffraction patterns for the $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ samples with $0.10 \leq z \leq 0.79$ (samples 4 and 11–14). The patterns for the samples with $z = 0.78$ and 0.73 are in-

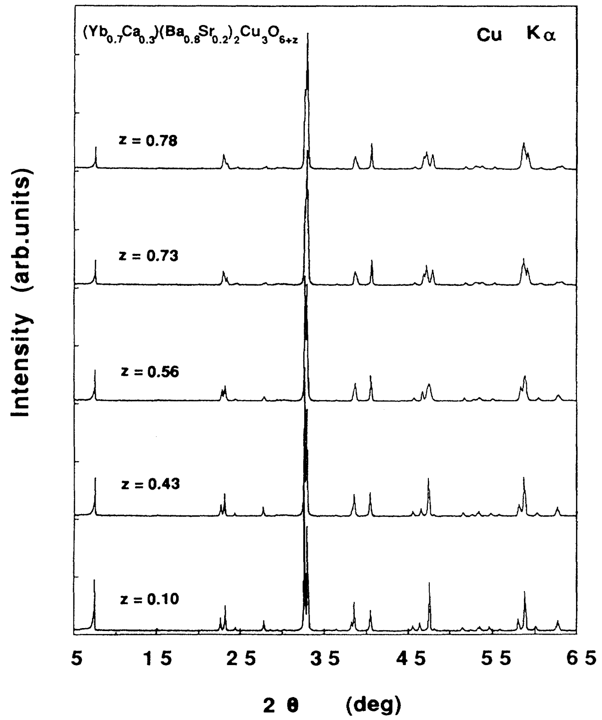

FIG. 4. X-ray powder diffraction patterns for $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ samples with various oxygen contents.

dexed for orthorhombic unit cells and those for the samples with $z=0.56$, 0.43, and 0.10 are indexed for tetragonal unit cells. The lattice constants of $(Yb_{0.9}Ca_{0.1})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ and $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ are summarized in Table I. The relationship between the lattice constants (a, b, and $c/3$, for the orthorhombic phase or a and $c/3$ for the tetragonal phase) and oxygen contents, $6+z$, are given in Fig. 5 for the two systems. The c axes linearly increase with decreasing oxygen content. It is seen in the figure that orthorhombic-tetragonal phase transitions occur around $(6+z)=6.6$ for both systems. This indicates that the orthorhombic-tetragonal structural phase transition in the 1:2:3 compound is mostly dependent on the oxygen content of the sample.

The temperature dependences of electrical resistivity for $(Yb_{0.9}Ca_{0.1})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ and $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ are shown in Figs. 6(a) and 6(b). Samples with high oxygen contents are metallic and exhibit fairly sharp superconducting transitions with $\Delta T_c(=T_c^{\text{on}}-T_c^{R=0})\sim 5$ K). Those with low oxygen contents such as $(Yb_{0.9}Ca_{0.1})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6.36}$ and $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6.10}$ are metallic only at high temperatures above 125 K and semiconductive at low temperatures, and they exhibited rather broad superconducting transitions with $\Delta T_c > 10$ K. The resistivities at 200 K for the $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ samples with $z=0.78$, 0.73, 0.56, 0.43, and 0.10 were 1.16×10^{-3}, 1.36×10^{-3}, 2.14×10^{-3}, 4.02×10^{-3} and 5.73×10^{-3} Ω cm, respectively. Thus, the resistivity in the normal state, i.e., at 200 K, increases with decreasing oxygen content. The zero-resistance temperatures ($T_c^{R=0}$) of the $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ samples were 40 K for $z=0.78$, 57 K for $z=0.73$, 80 K for $z=0.56$, 58 K for $z=0.43$, and 36 K for $z=0.10$. Thus, as the oxygen content decreases, $T_c^{R=0}$ exhibits maximum.

The temperature dependences of the dc magnetic susceptibility for $(Yb_{0.9}Ca_{0.1})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ and $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ are shown in Fig. 7. Both samples exhibited bulk superconductivity. The magnetic superconducting transition temperatures (T_c^{mag}) are summarized in Table I. The relationship between (T_c^{mag}) and the oxygen content is showm in Fig. 8. The T_c^{mag}'s are in good agreement with T_c's electrically determined. For the system with $x=0.1$, as the oxygen content $6+z$ is decreased, T_c shows a maximum around $(6+z)=6.69$ and decreases down to 48 K at $(6+z)=6.36$. For the system with $x=0.3$, T_c also exhibits a maximum around $(6+z)=6.56$ and decreases down to 40 K at $(6+z)=6.10$. In the

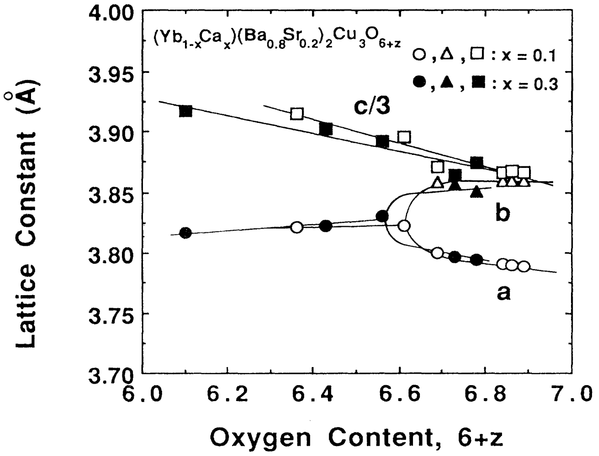

FIG. 5. Relationship between the lattice constants and the oxygen content in $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ with $x=0.1$ and 0.3.

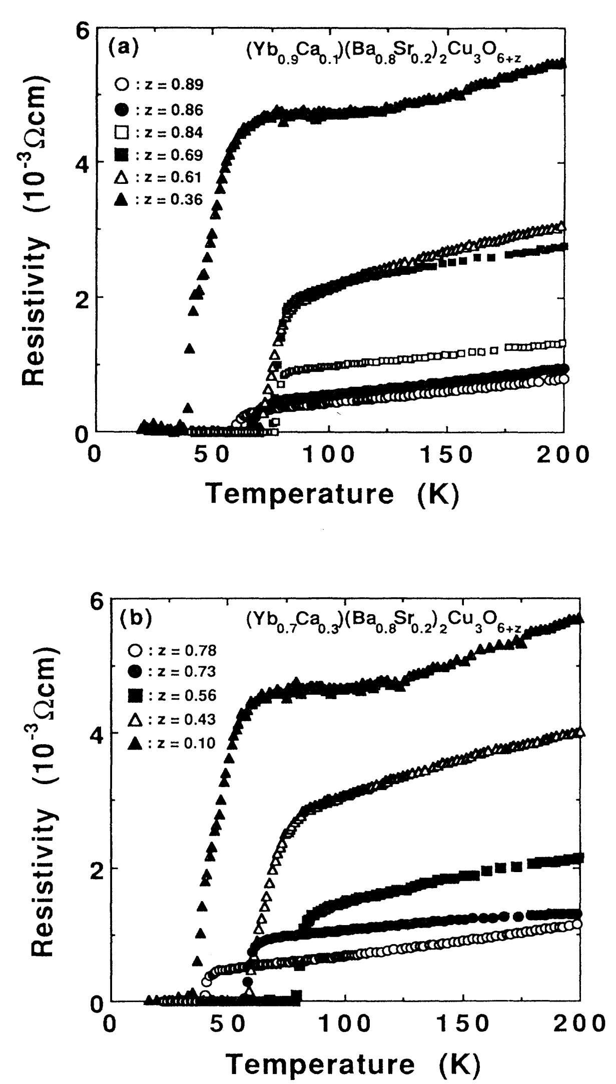

FIG. 6. Temperature dependence of electrical resistivity for $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ with $x=0.1$ and 0.3.

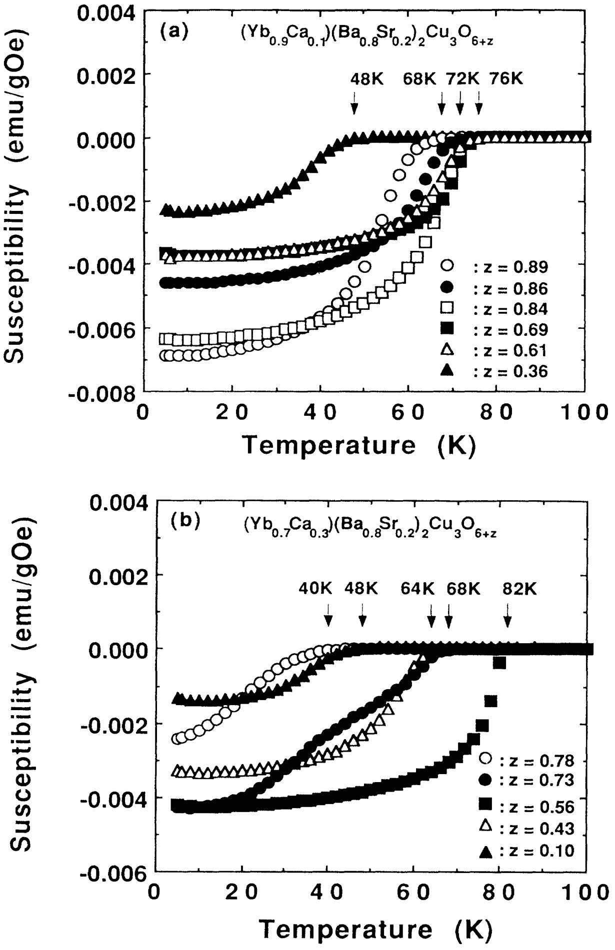

FIG. 7. Temperature dependence of dc magnetic susceptibility for $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ with $x = 0.1$ and 0.3.

$(Yb_{0.9}Ca_{0.1})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ system, the maximum T_c was obtained for an orthorhombic compound with $(6+z)=6.69$. In the $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ system, the maximum T_c was recorded for a tetragonal compound with $(6+z)=6.56$. Thus, T_c maxima of the system with different Ca contents were found at different oxygen contents.

IV. DISCUSSION

The Ca content (x), oxygen content $(6+z)$, average copper valence $[V(\mathrm{Cu})]$, and magnetic superconducting transition temperature (T_c^{mag}) are summarized in Table II. T_c apparently depends on both the Ca content and the oxygen content. For samples 1–5, post annealed at $P(O_2)=400$ atm, as the Ca content increases, T_c linearly decreases, while the average copper valence $V(\mathrm{Cu})$ has a maximum peak at $x=0.2$. Therefore, T_c of the present 1:2:3 superconducting compounds is not simply proportional to the average valence of Cu.

Tokura *et al.*[11] proposed a model that T_c of the 1:2:3 superconductor depends on the concentration of mobile holes in the CuO_2 sheet contained in the Y-CuO_2-BaO block. The mobile hole concentration in the CuO_2 sheet, p_{sheet}, is calculated as follows. First, the average hole concentration per Cu, p, is calculated from the average Cu valence

$$p = V(\mathrm{Cu}) - 2 \ ,$$

and the critical hole concentration per Cu, p_c, is estimated from the empirical relation

$$p_c = -2.21 + 0.34(6+z) \ .$$

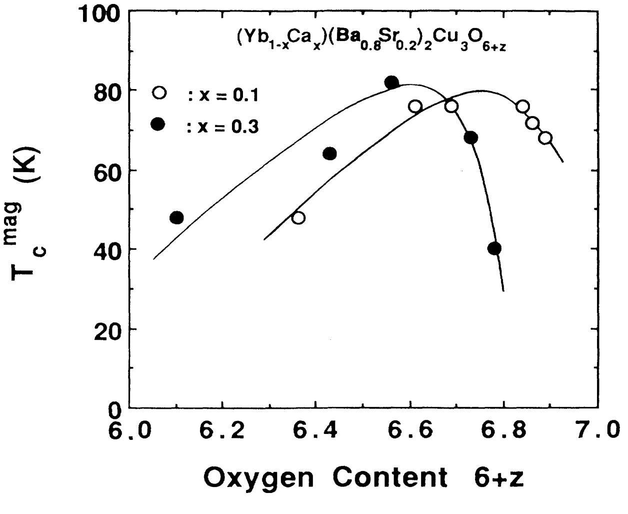

FIG. 8. Relationship betweeen the oxygen content and the magnetic T_c for $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ with $x = 0.1$ and 0.3.

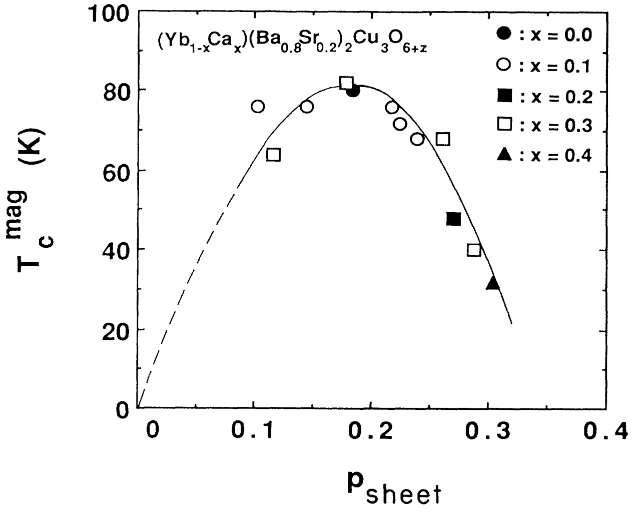

FIG. 9. Relationship between T_c and mobile hole concentration in the CuO_2 sheet, p_{sheet} for the $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ systems with $x = 0.1$ and 0.3.

TABLE II. Composition, average copper valence, hole concentrations and magnetic superconducting transition temperature of $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$.

Sample number	Composition x	$(6+z)$	$V(Cu)$[a]	Hole concentration p_c[b]	p_{sheet}[c]	T_c^{mag} (K)
1	0.0	6.875	2.250	0.128	0.184	80
2	0.1	6.885	2.290	0.131	0.239	68
3	0.2	6.845	2.297	0.117	0.270	48
4	0.3	6.780	2.287	0.095	0.288	40
5	0.4	6.712	2.275	0.072	0.304	32
6	0.1	6.858	2.272	0.122	0.225	72
7	0.1	6.843	2.262	0.117	0.218	76
8	0.1	6.692	2.161	0.065	0.144	76
9	0.1	6.609	2.106	0.037	0.103	76
10	0.1	6.364	1.943	−0.046	−0.017	48
11	0.3	6.727	2.251	0.077	0.261	68
12	0.3	6.558	2.139	0.020	0.179	82
13	0.3	6.431	2.054	−0.024	0.116	64
14	0.3	6.100	1.833	−0.136	−0.047	48

[a] $V(Cu)$ average copper valence $V(Cu)=[\{x-7+2(6+z)\}/3]$.

[b] p_c, critical hole concentration per Cu $[p_c=-2.21+0.34(6+z)]$ (Ref. 11).

[c] p_{sheet}, hole concentration per Cu at the sheet site $[p_{sheet}=3(p-p_c)/2]$.

The average hole concentration p relates to the hole concentration in the CuO_z chain (plane), p_{chain}, and the hole concentration in the CuO_2 sheet, p_{sheet}:

$$p=(p_{chain}+2p_{sheet})/3 \ .$$

When $p=p_c$, p_{sheet} is zero. Thus, p_{chain} is calculated

$$p_{chain}=3p_c \ .$$

Consequently, p_{sheet} is obtained:

$$P_{sheet}=3(p-p_c)/2 \ .$$

The calculated values for p_c and p_{sheet} are summarized in Table II. T_c^{mag}'s are plotted against p_{sheet} in Fig. 9. As the p_{sheet} increases, T_c shows a maximum peak at $p_{sheet}=0.18$ and decreases down to 32 K at $p_{sheet}=0.304$. The shape of this T_c^{mag} versus p_{sheet} curve is similar to that of the one obtained for the $La_{2-x}Sr_xCuO_4$ system.

The average valence of Cu for the samples with low oxygen contents, such as $(Yb_{0.9}Ca_{0.1})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6.36}$ and $(Yb_{0.7}Ca_{0.3})(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6.10}$, is lower than 2, and the calculated hole concentration in the CuO_2 sheet is also minus. Nevertheless, these samples are superconducting. Therefore, we concluded that the present estimation[11] of the mobile hole concentration in the CuO_2 sheet was not adequate for the system with low oxygen content. This may be due to the ordering of oxygen on the CuO_z chain site.[12,13]

V. SUMMARY

The $(Yb_{1-x}Ca_x)(Ba_{0.8}Sr_{0.2})_2Cu_3O_{6+z}$ $(0\le x\le 0.4)$ solid solutions were synthesized. The superconducting transition temperatures (T_c's) of the samples post annealed at $P(O_2)=400$ atm ranged from 80 to 32 K depending on the Ca content. As the oxygen content, $6+z$, of $(Yb,Ca)(Ba,Sr)_2Cu_3O_{6+z}$ decreased, T_c showed a maximum peak at $p_{sheet}=0.18$. The curve of T_c versus the concentration of mobile holes in the CuO_2 sheet exhibited a similar shape as the one reported for the $La_{2-x}Sr_xCuO_4$ system.

ACKNOWLEDGMENTS

We thank T. Kawano for his help in a Coulometric titration. A part of this work was supported by New Energy and Industrial Technology Development Organization as a part of the program for R&D Basic Technology for Future Industries.

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