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Preparation and properties of superconducting $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$

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We have prepared single-phase or near-single-phase $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ ($0 \le x \le 0.4$) samples by means of a high-oxygen-pressure technique using an O_2 hot isostatic pressing. All the lattice constants, *a*, *b*, and *c*, of $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ monotonically decreased with increasing Sr content. The superconducting transition temperatures of these samples were nearly constant, being around 80 K, while the T_c's of $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ ($z \sim 7$) samples decreased with increasing Sr content. When Y in $Y(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$ was partially substituted by Ca, the superconducting critical temperature increased to near 90 K.

INTRODUCTION

The $YBa_2Cu_4O_8$ (1:2:4) phase was first discovered as lattice defects in the $YBa_2Cu_3O_z$ (1:2:3) phase by transmission electron microscopy[1] and artificially prepared in a thin-film form.[2,3] Later, Karpinski *et al.*[4] and Morris *et al.*[5] independently synthesized bulk 1:2:4 samples by a high-oxygen-pressure technique. These samples exhibited superconducting transitions at around 80 K. Cava *et al.*[6] were successful in synthesizing the 1:2:4 phase in a powder form under one atmospheric oxygen pressure by utilizing a catalyst such as alkali-metal carbonates. Neutron[7] and x-ray diffraction[8,9] studies revealed that the 1:2:4 compound has a layered perovskite structure with two different kinds of Cu sites, Cu(2) sites forming a $Cu(2)O_2$ plane between a Y plane and a Ba plane and Cu(1) sites forming double Cu-O chains running along the *b* axis between two Ba planes. The 1:2:4 compound has excellent thermal stability of oxygen content up to 800 °C and has no orthorhombic-tetragonal structural phase transition at an elevated temperature.[4] Recently, Miyatake *et al.*[10] reported an increase of T_c to 90 K for a 1:2:4 compound with Ca doped and explained the increase of T_c using the concept of an average charge *p* per $[\text{Cu-O}]^{p+}$ unit cell, as proposed by Torrance *et al.*[11] However, no further data have been available to date to analyze the mechanism for the increase in T_c by a Ca substitution in the 1:2:4 compound.

In this paper, we study the effect of Sr substitution for Ba in the $YBa_2Cu_4O_8$ (1:2:4) compound on the crystallographic and superconducting properties. The results obtained will be compared with those for a $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ compound with $z \sim 7$. Furthermore, we test the Ca doping effect on T_c of $Y(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$.

EXPERIMENTAL

The 1:2:4 samples were prepared employing a solid-state reaction method and a hot isostatic pressing (HIP) technique using a mixture of $(Ar+O_2)$ gas. High-purity (99.9%) powders of Y_2O_3, $CaCO_3$, $Ba(NO_3)_2$, $Sr(NO_3)_2$ and CuO were mixed in ethanol by means of a ball mill and the mixed powder was calcined at 900 °C in O_2 gas flow for 24 h. The calcined powder was compacted and sintered at 900 °C in flowing O_2 gas. The resultant ceramics were annealed in a mixed gas [Ar (80%)$-O_2$ (20%)] of 100 MPa at 1000 °C. The $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ (1:2:3) samples with $z \sim 7$ were prepared for reference by an ordinary solid-state reaction method.

The phases present and the lattice constants were determined by powder x-ray diffraction using Cu-$K\alpha$ radiation. For refined measurements, a curved graphite monochromator was placed in the scattering beam path. The oxygen content was analyzed by an inert gas fusion nondispersive ir method (HORIBA: model EMGA-650).[12] Electrical resistivity was measured by a conventional dc four-probe method. Magnetic susceptibility was measured by a SQUID magnetometer (Quantum Design: Model MPM). Thermogravimetric measurements were performed for pulverized samples. The procedures for thermal analyses were described in detail elsewhere.[13]

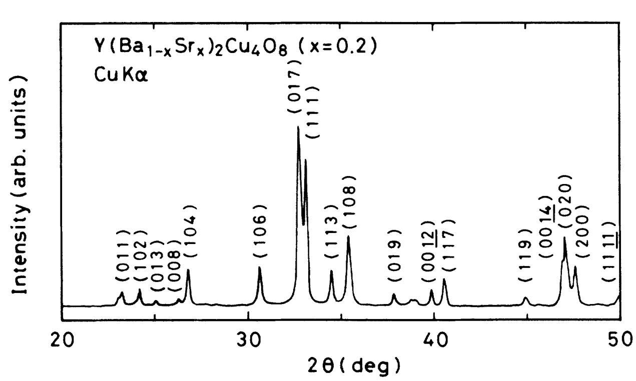

FIG. 1. X-ray diffraction pattern of a sample with $x = 0.2$ of the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ system.

TABLE I. Sr content (x), oxygen content (z), lattice constants, and superconducting transition temperatures in the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ system. The quantity, $(b-a)/a$, represents the orthorhombicity of the crystal lattice. (Numbers in the parentheses indicate standard deviations.)

Sample	Composition		Lattice constants				T_c (K)	
number	x	z	a (Å)	b (Å)	c (Å)	$[(b-a)/a]\times 10^3$	T_c^{on}	$T_c^{R=0}$
1	0.00	7.8	3.836(1)	3.872(1)	27.224(1)	9.3	80	75
2	0.05	7.9	3.823(1)	3.868(1)	27.194(1)	11.7	81	75
3	0.10	7.9	3.820(1)	3.866(1)	27.176(1)	12.2	82	74
4	0.20	7.9	3.805(1)	3.862(1)	27.122(1)	15.1	82	76
5	0.30	7.8	3.802(1)	3.860(1)	27.068(1)	15.4	83	74
6	0.40	7.9	3.799(1)	3.856(1)	27.021(1)	15.1	83	75

RESULTS AND DISCUSSION

All the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples with $0 \le x \le 0.4$ were of single phase or near single phase according to powder x-ray diffraction analyses. Figure 1 shows the x-ray diffraction pattern of a 1:2:4 sample with $x=0.2$. The diffraction peaks were successfully indexed with an orthorhombic unit cell with the lattice constants of $a=3.805$, $b=3.862$, and $c=27.122$ Å. In the samples with $x \ge 0.5$, a secondary impurity phase of $BaCuO_2$ was formed. The oxygen contents of the samples were analyzed and the results were given in Table I: the oxygen contents were nearly constant being at $z \sim 8.0$ for all the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples. For the $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ system, single-phase samples were successfully synthesized for x between $x=0$ and $x=0.6$. The measured oxygen contents z of the 1:2:3 samples were given in Table II. The z values for the $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ samples were about 6.9 being independent of the Sr content.

The lattice constants of $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples are given in Table I and are plotted against the Sr content x in Fig. 2. The lattice constants a, b, and c, of the sample with $x=0$, i.e., $YBa_2Cu_4O_8$, were 3.836, 3.872, and 27.224 Å, respectively. These values are in good agreement with previous reported data.[7] Figure 2 shows that the lengths of a, b, and c axes monotonically decreased with increasing Sr content x from 0 to 0.4. The dependence of the a, b, and c axis lengths on the Sr content was also observed for the $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ system. The measured lattice constants of $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ samples are given in Table II and the lengths of a, b, and c axes are plotted in Fig. 2 for comparison. These lattice constants of the $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ system are in good agreement with our previous data.[14] The decrease in the lattice constants of the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ and $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ samples with increasing Sr content was attributed to the difference in the ionic radii (for C.N.=10) (Ref. 15) of Ba^{2+}(1.52 Å) and Sr^{2+}(1.36 Å). Tables I and II, and Fig. 2 show that the orthorhombicity $(b-a)/a$ of the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ system increases with increasing Sr content, while that of the

TABLE II. Sr content (x), oxygen content (z), lattice constants, and superconducting transition temperatures in $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ systems. The quantity, $(b-a)/a$, represents the orthorhombicity of the crystal lattice. (Numbers in the parentheses indicate standard deviations).

Sample	Composition		Lattice constants				T_c (K)	
number	x	z	a (Å)	b (Å)	c (Å)	$[(b-a)/a]\times 10^3$	T_c^{on}	$T_c^{R=0}$
1	0.00	6.9	3.823(1)	3.892(1)	11.684(1)	17.8	94	91
2	0.10	6.8	3.815(1)	3.883(1)	11.656(1)	17.4	94	87
3	0.20	6.8	3.805(1)	3.875(1)	11.624(1)	17.9	91	86
4	0.30	6.8	3.803(1)	3.869(1)	11.610(1)	17.1	88	84
5	0.40	6.8	3.792(1)	3.859(1)	11.578(1)	17.6	88	84
6	0.50	6.8	3.792(1)	3.850(1)	11.553(1)	15.0	85	82
7	0.60	6.8	3.781(1)	3.842(1)	11.527(1)	16.0	83	81

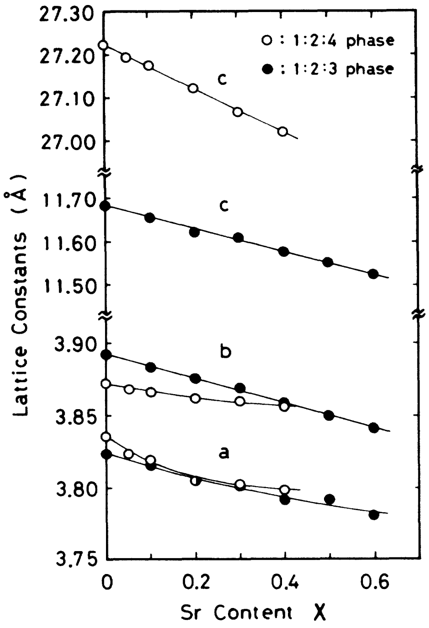

FIG. 2. Lattice constants, *a*, *b*, and *c*, of $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ and $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ ($z \sim 7$) with respect to the Sr content *x*.

$Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ system was little affected by a change in the Sr content.

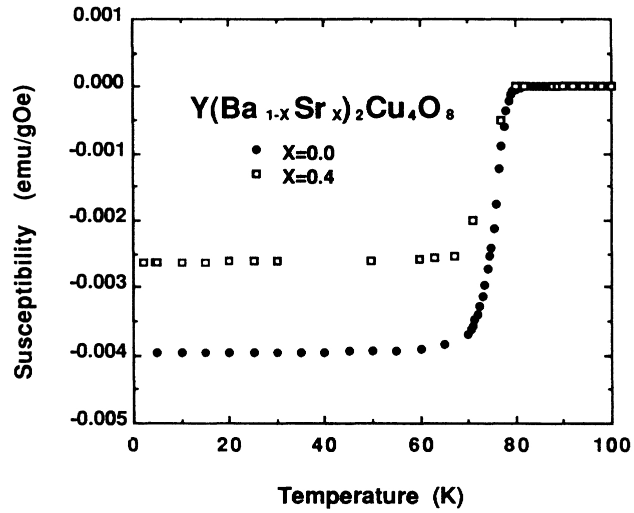

FIG. 4. Temperature dependence of dc magnetic susceptibility of $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples with $x=0.0$ and 0.4. The measurements were performed by decreasing temperature under a constant field of 10 Oe.

Figure 3 shows the temperature dependence of electrical resistivity of the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples. The sample with $x=0$ shows metallic temperature dependence of resistivity and a sharp superconducting transition at $T_c^{\mathrm{on}}=80$ K and $T_c^{R=0}=75$ K. These T_c's are in good agreement with a previous reported value of magnetically determined superconducting transition temperature ($T_c^{\mathrm{mag}} \sim 80$ K).[4,5] The samples with $x=0.05$, 0.10, 0.20, 0.30, and 0.4 show similar temperature dependence of resistivity and show superconducting transition at around 80 K. The sample with $x=0.5$ shows superconducting transition at about 80 K but the resistivity at normal state is higher than those of the other samples. This is because the sample with $x=0.5$ contained impurity second phase. Figure 4 shows the temperature dependence of dc magnetic susceptibility of the samples with $x=0.0$ and 0.4. The measurements were performed by decreasing temperature under a constant field of 10 Oe. These two samples exhibited bulk superconductivity

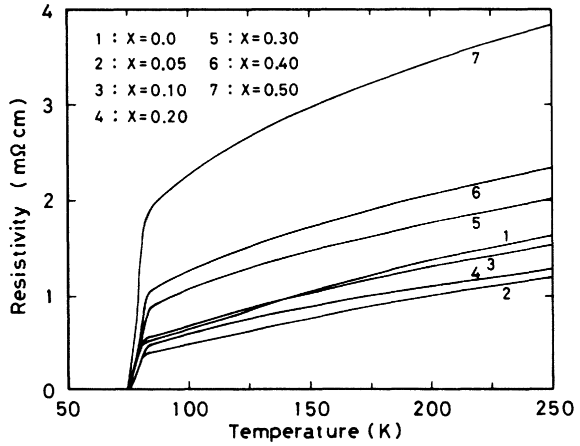

FIG. 3. Temperature dependence of electrical resistivity of $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples with $x=0.0$, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5.

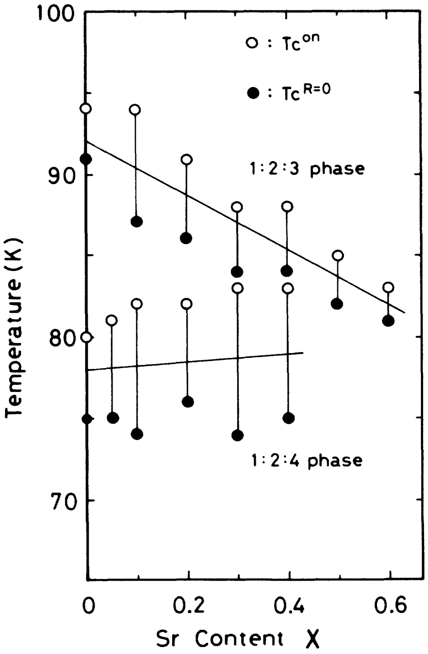

FIG. 5. Superconducting transition temperature vs Sr content *x* for two different phases: $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ and $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ ($z \sim 7$).

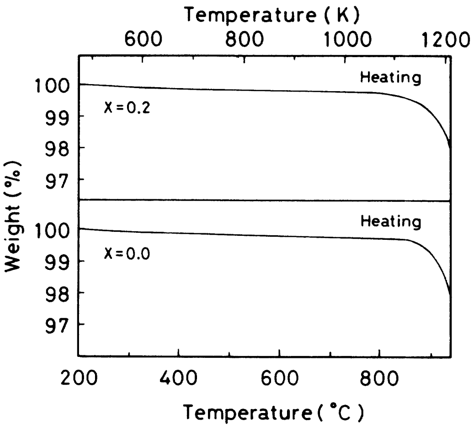

FIG. 6. Thermogravimetric (TG) curves of samples with $x=0.0$ and 0.2 of the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ system. The measurements were made with a heating rate of 10 °C/min at an O_2 gas flow rate of 100 cm^3/min.

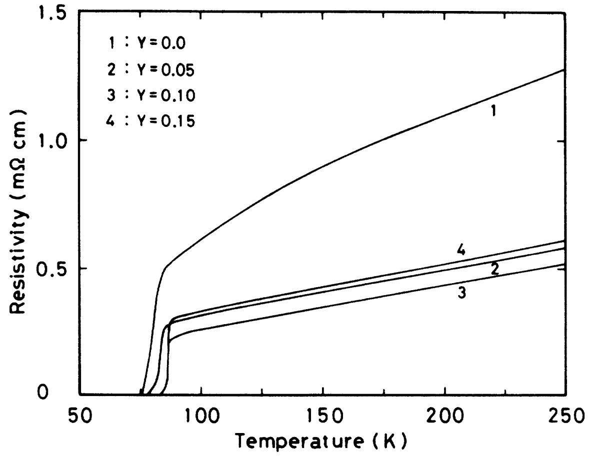

FIG. 7. Temperature dependence of electrical resistivity of $(Y_{1-y}Ca_y)$ $(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$ samples with $y=0.0$, 0.05, 0.10, and 0.15.

and the susceptibility signals at 10 K were larger than 25% of a full Meissner effect. The superconducting transition temperatures were 81 and 80 K for the sample with $x=0.0$ and 0.4, respectively. These values for the magnetic T_c are in good agreement with those determined by electrical resistivity measurements, which are tabulated in Table I and plotted against the Sr content x in Fig. 5. The open circles show the superconducting onset temperature and the solid circles show the zero resistance temperature. Figure 5 shows that the T_c's of the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples were unaltered when the Sr content, x, was varied from 0 to 0.4. This is contrary to the case of the $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ system, in which T_c was monotonically lowered from 92 to 82 K with increasing Sr content x from 0 to 0.6, as demonstrated in Fig. 5. The magnitude of the gradient, dT_c/dx, was as high as 15 K.

Figure 6 shows thermogravimetric curves for the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ samples with $x=0$ and 0.2. The measurements were made in a temperature range between 200 and 940 °C with a heating rate of 10 °C/min at an O_2 gas flow rate of 100 cm^3/min. The TG curves of the two samples with $x=0.0$ and 0.2 are not significantly different. This result indicates that the oxygen content in this Sr substituted 1:2:4 sample is thermally stable up to a significantly high temperature (~850 °C) as was the case of the sample without Sr.[4,10]

In order to study the effect of Ca substitution for Y in the $Y(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$ compound on the crystallographic and superconducting properties, samples of nominal compositions, $(Y_{1-y}Ca_y)$ $(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$, were synthesized. The samples with $0 \leq y \leq 0.1$ were of single phase or near single phase, and the sample with $y=0.15$ was found to contain $BaCuO_2$ as a secondary phase. The oxygen contents z and crystal data, a, b, c, and $(b-a)/a$, were summarized in Table III. This table shows that the oxygen content of $Y(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$ is not affected by Ca doping. The c axis lengthens slightly but the a and b axes remain more or less unchanged as the Ca content increased. The orthorhombicity, $(b-a)/a$, was decreased with increasing the Ca content.

Figure 7 shows the temperature dependence of electrical resistivity of the $(Y_{1-y}Ca_y)$ $(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$ samples with $y=0.0$, 0.05, 0.1, and 0.15. The values of T_c^{on} and $T_c^{R=0}$ measured are given in Table III. As the amount of doped Ca increased, the transition temperature was raised. For the sample with $y=0.1$, the superconducting onset temperature was 87 K and the resis-

TABLE III. Ca content (y), oxygen content (z), lattice constants, and superconducting transition temperatures in $(Y_{1-y}Ca_y)$ $(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$. The quantity, $(b-a)/a$, represent the orthorhombicity of the crystal lattice. (Numbers in the parentheses indicate standard deviations.)

Sample	Composition		Lattice constants				T_c (K)	
number	y	z	a (Å)	b (Å)	c (Å)	$[(b-a)/a]\times 10^3$	T_c^{on}	$T_c^{R=0}$
1	0.00	7.8	3.805(1)	3.862(1)	27.122(1)	15.1	82	76
2	0.05	7.8	3.813(1)	3.861(1)	27.130(1)	12.6	85	79
3	0.10	7.8	3.812(1)	3.859(1)	27.155(1)	12.3	87	84

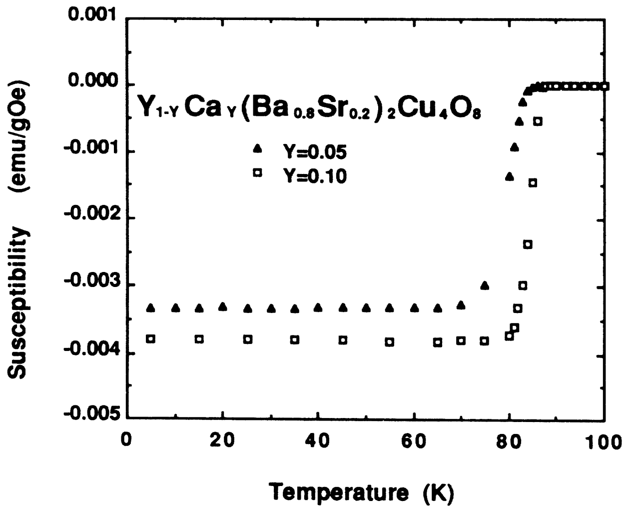

FIG. 8. Temperature dependence of dc magnetic susceptibility of $(Y_{1-y}Ca_y)$ $(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$ samples with $y=0.05$ and 0.1. The measurements were performed by decreasing temperature under a constant field of 10 Oe.

tance reached zero at 84 K. These values are as high as those for $(Y_{0.9}Ca_{0.1})Ba_2Cu_4O_8$.[9] The temperature dependence of dc magnetic susceptibility of $(Y_{1-y}Ca_y)$ $(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$ sample is shown in Fig. 8. All the samples showed bulk superconductivity and susceptibility signals at 10 K were larger than 25% of a full Meissner effect. The superconducting transition temperatures were 85 and 87 K for the sample with $y=0.05$ and 0.10. Thus, T_c^{mag} for $Y(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$ increased to 87 K by Ca doping.

In summary, samples of $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ $(0\leq x\leq 0.5)$ and $(Y_{1-y}Ca_y)$ $(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$ $(0\leq y\leq 0.15)$ were prepared in a mixture of Ar and O_2 gases by a hot isostatic pressing technique. The lattice constants, a, b, and c, of $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ as well as $Y(Ba_{1-x}Sr_x)_2Cu_3O_7$ system monotonically decreased with increasing Sr content, x. The superconducting transition temperatures of $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ were nearly constant being around 80 K, while T_c's of $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ $(z\sim 7)$ samples decreased with increasing Sr content from 91 K for $x=0.0$ to 80 K for $x=0.6$. The magnitude of T_c for $Y(Ba_{0.8}Sr_{0.2})_2Cu_4O_8$ was increased to near 90 K by Ca doping.

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