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High-T_c Superconductivity in Copper Oxide Compounds

(high-T_c superconductivity/Y-Ba-Cu-O system/substitution effect)

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The effect of substitution of Sr, Cs, Zn, Ni, F, Cl, S, Se or I for Y, Ba, Cu or O on the superconducting transition in the Y-Ba-Cu-O system has been investigated. It was found that the partial replacement of Cu by Ni or Zn strongly depresses the superconducting transition temperature. An extremely sharp transition was observed in $YBa_2Cu_3O_y$ samples when they were sintered in iodine gas and then annealed in air or flowing oxygen. The result suggests that the Cu and O ions play important roles in the occurrence of the high-T_c superconductivity. An anomalous resistivity change, reminiscent of a superconducting transition, was observed around 180 K in a $YBa_2Cu_3O_y$ sample which was sintered in selenium gas followed by annealing in oxygen gas.

INTRODUCTION

In 1986, Bednorz and Müller[1] discovered a La-Ba-Cu-O system which showed an abrupt decrease in the resistivity in the 30 K range, suggesting the onset of superconductivity. Subsequently, magnetic susceptibility measurements by Bednorz et al.[2] and Uchida et al.[3] revealed that the resistivity transition was due to superconductivity of bulk nature. The crystal structure of the superconducting phase was identified to be a layered perovskite, K_2NiF_4 structure.[4]

The accomplishment of high-temperature superconductivity is of immense scientific and technological importance. Since the historical discovery by Bednorz and Müller, many efforts have been done to raise the superconducting transition temperature (T_c). A superconducting transition in the 90 K range was reported by Wu et al.[5] in a mixed-phase Y-Ba-Cu-O system. The identified superconducting phase has an orthorhombic oxygen defect perovskite structure with composition $YBa_2Cu_3O_y$ $(6.5 < y < 8)$.[6]

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Quite recently, a phenomenon was reported which might imply the occurrence of superconductivity at room temperature. However, those samples were unstable and could not be well characterized.[7]

In this paper, we study the influence of various chemical substituents in the place of Y, Ba, Cu or O in the Y-Ba-Cu-O system on the superconducting transition and the normal state resistivity behaviors. This work was begun to obtain higher T_c and some information about the possible mechanism of high-T_c superconductivity.

SAMPLE PREPARATION AND MEASUREMENT

The samples were synthesized by the solid-state reaction[5] of appropriate amounts of powders (Y_2O_3, Sc_2O_3, $BaCO_3$, $SrCO_3$, Cs_2CO_3, CuO, ZnO, NiO,

Table I. Superconducting data for materials derived from the Y-Ba-Cu-O system

Compound	$T_c^{90\%}$ (K)	$T_c^{50\%}$ (K)	$T_c^{10\%}$ (K)	ΔT_c (K)	ρ(300K) ($\mu\Omega$m)
$(Y_{0.6}Ba_{0.4})_2CuO_y$	95.5	88.9	87.4	8.1	450
$(Y_{0.6}Ba_{0.4})_2Cu_{0.9}Ni_{0.1}O_y$	67.2	62.4	58.8	8.4	770
$(Y_{0.6}Ba_{0.4})_2Cu_{0.9}Zn_{0.1}O_y$	58.6	55.6	46.9	11.7	3600
$(Y_{0.6}Ba_{0.4})_2Cu_{0.9}O_y$	91.9	84.3	—[a]	—[a]	96000
$Y_{0.7}Cs_{0.3}Ba_2Cu_3O_y$	90.1	88.5	86.3	3.7	1800
$Y(Ba_{0.7}Cs_{0.3})_2Cu_3O_y$	95.6	90.8	89.4	6.3	290
$YBa_2(CuO_{0.9}S_{0.1})_3O_y$	90.5	90.0	89.2	1.3	370
$YBa_2(CuO_{0.9}F_{0.1})_3O_y$	94.5	91.3	88.1	6.4	850
$YBa_2(CuO_{0.7}F_{0.3})_3O_y$	88.9	86.0	83.8	5.1	89
$YBa_2(CuO_{0.9}Cl_{0.1})_3O_y$	—	—	—	—	insulator
$YBa_2(CuO_{0.7}Cl_{0.3})_3O_y$	—	—	—	—	insulator
$YSr_2Cu_3O_y$	—	—	—	—	insulator
$Sc_2Ba_2Cu_3O_y$	—	—	—	—	insulator
$Y_{0.7}Sc_{0.3}Ba_2Cu_3O_y$	90.9	90.0	88.1	2.8	41
$YBa_2CaCu_3Cl_2O_y$	—	—	—	—	insulator
$YBa_2Cu_3Cl_2O_y$	—	—	—	—	insulator
$YSr_2Cu_3FO_y$	—	—	—	—	insulator
$YSr_2Cu_3F_2O_y$	—	—	—	—	insulator
$YSr_2Cu_3F_{0.2}O_y$	—	—	—	—	insulator
$YSr_2Cu_3F_{0.6}O_y$	—	—	—	—	insulator
$YBa_2Cu_3O_y$[b]	91.8	91.4	91.0	0.8	260
$YBa_2Cu_3O_y$[c]	91.6	90.9	89.4	2.1	1600
$YBa_2Cu_3O_y$[d]	91.9	89.4	83.8	8.1	190

a) The resistivity did not decrease to zero down to 28 K.
b) The sample was sintered in iodine gas and then annealed in air.
c) The sample was sintered in sulfur gas and then annealed in air.
d) The sample was sintered in selenium gas and then annealed in flowing oxygen.

CuF_2, CuS, $CuCl_2 \cdot xH_2O$).

The mixtures were heated in air for 6–10 h at 900 °C, ground and cold pressed with 3–4 kbar/cm^2 to form pellets of 1-cm diameter and 0.2-cm thickness. The pellets were sintered in air at 950 °C for 15–24 h, and cooled to room temperature slowly at a rate of 0.5 °C/min. Synthesized materials are listed in table I.

The $YBa_2Cu_3O_y$ samples were prepared first by sintering in quartz tubes which were closed with some amount of sulfur, selenium or iodine and then by re-annealing in air or flowing oxygen at 950 °C for 15–24 h. The color of the sulfur- or selenium- annealed samples was dark pink and that of the iodine-annealed samples was a mixture of purple and green. The colors of both compounds changed to black after re-annealing in air or flowing oxygen.

Samples with the nominal composition $YBa_2Cu_3O_y$ and $Y_{0.7}Sc_{0.3}Ba_2Cu_3O_y$ were examined by X-ray powder diffraction using Cu-Kα radiation. The X-ray diffraction pattern for $Y_{0.7}Sc_{0.3}Ba_2Cu_3O_y$ is represented in Fig. 1. The pattern corresponds to that for $YBa_2Cu_3O_y$[8], which confirms that the sample is single phase. The X-ray results showed that the samples with the other compositions were multi-phase.

Bar samples of dimensions (typically 1.5×1×3 mm^3) were cut from the

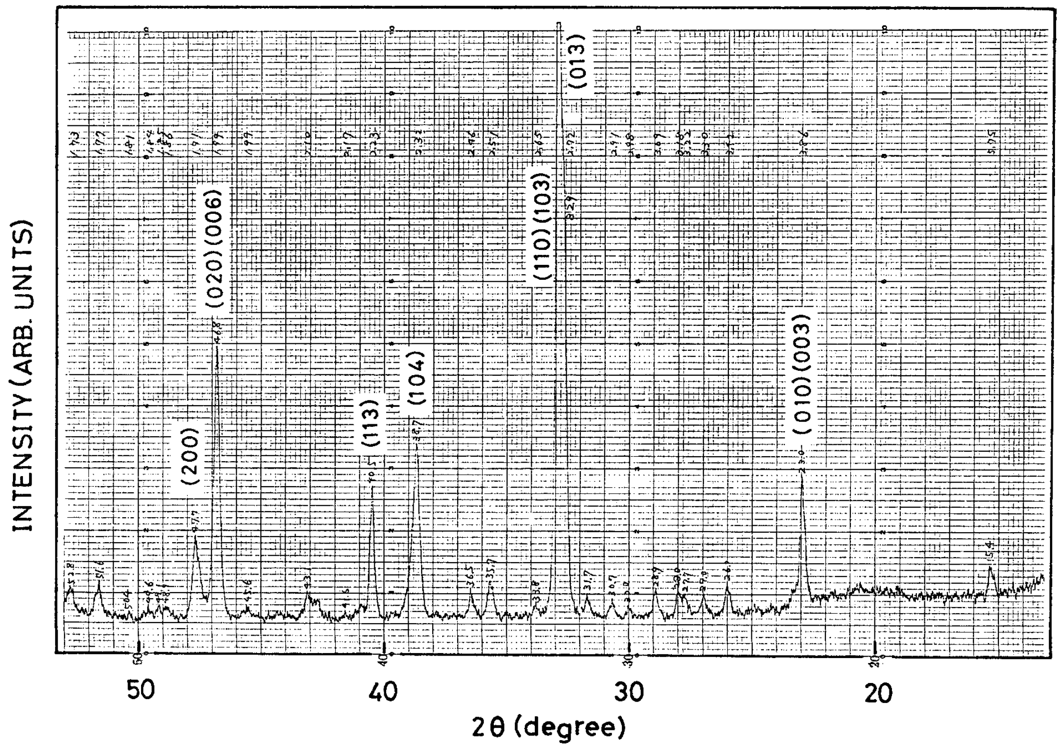


Fig. 1. X-ray diffraction pattern for a $YBa_2Cu_3O_y$ sample which was sintered in iodine gas and re-annealed at 950 °C in air.

sintered pellets.

A dc, four-terminal technique was employed for the resistivity measurements. The sample was mounted in a cryostat and was cooled by a closed refrigeration system (Osaka Oxygen Industries Co.: Cryo-Mini D). A Au (+0.07 at% Fe)—chromel thermocouple was used to measure the temperature of the sample. The resistivity was measured using an automatic digital recording system[9] including a digital volt-meter (keithley: model 195) driven by a 16-bit microcomputer.

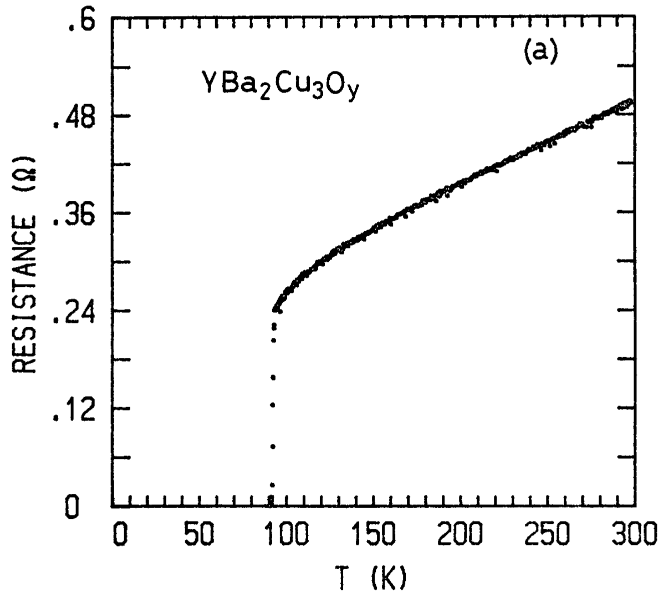
EXPERIMENTAL RESULTS AND DISCUSSION

Table I summarizes the superconducting data for the investigated compounds which were derived from the Y-Ba-Cu-O system. The onset temperature of the superconducting transition corresponds to the point where the resistivity starts to drop significantly with decreasing temperature. The transition width is defined as the temperature difference between $T_c^{90\%}$ and $T_c^{10\%}$.

(1) $YBa_2Cu_3O_y$

We attempted to sinter the $YBa_2Cu_3O_y$ samples in sulfur, selenium or iodine gas in order to replace oxygen by sulfur, selenium or iodine. However, we found that all the samples were insulators. According to X-ray analysis, various phases were identified: $Cu_2Y_2O_5$, Cu, CuO, $BaCO_3$ and/or Y_2O_3. Then, we tried to re-anneal the samples for 20 h at 950 °C in air or flowing oxygen. The additional heating made the iodine- or selenium-annealed samples metallic. X-ray measurements revealed the presence of $Cu_2Y_2O_5$ phase in addition to $YBa_2Cu_3O_y$ phase in the sample which was sintered in iodine gas and re-annealed in air. Metallic conductivity was also recovered in some of the sulfur-annealed $YBa_2Cu_3O_y$ samples by this additional treatment. It is considered that the oxygen is released from the sample during sintering and reabsorbed by the sample during re-annealing. This result stresses the role of oxygen in the establishment of the high-T_c superconductivity.

Figure 2 shows that the $YBa_2Cu_3O_y$ sample which was annealed in iodine gas and then in air or flowing oxygen gas exhibits an extremely sharp transition with the transition width $\Delta T_c \sim 0.8$ K. Sintered samples are described as assemblies of superconducting grains which are coupled through nonstoichiometric interface materials.[2] We observed that the surfaces of the iodine-annealed samples were eroded by iodine gas. This fact and the porous nature of the ceramic sample suggest that the sharp transition is due to the removal of the inhomogeneous surface layers by the reaction



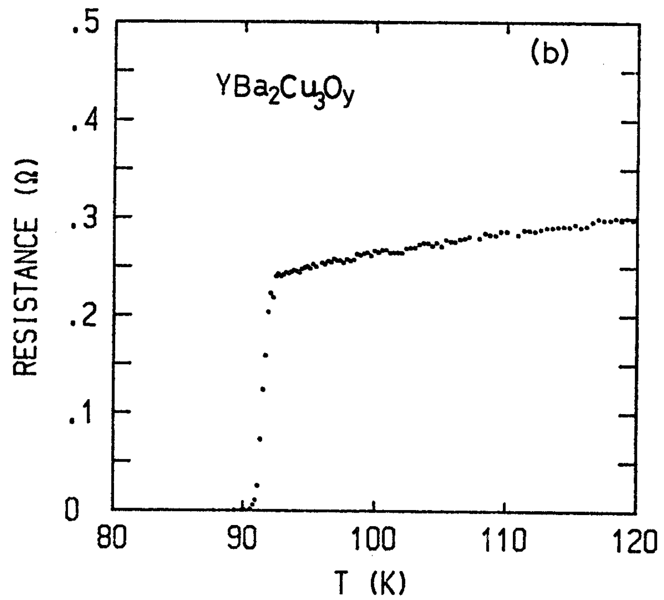


Fig. 2. (a) Temperature dependence of the resistance for a $YBa_2Cu_3O_y$ sample which was sintered in iodine gas and re-annealed at 950 °C in air. (b) Expansion of the region near T_c.

with iodine. The $Cu_2Y_2O_5$ phase does not seem to affect the transition and probably occupies the interior of the grains. It is pointed out that, with decreasing temperature, the resistivity starts to deviate from the linear curve around 180 K and the resistivity suddenly drops at $T_c^{onset} = 92.2$ K. (see Fig. 2) The rounding in the resistivity vs temperature curve was recently ascribed to the thermodynamic superconducting fluctuation.[10]

Figure 3 shows the resistive behavior of a sample which was sintered in selenium gas and then re-annealed in flowing oxygen. We notice a sharp decrease of the resistivity around 180 K. It is possible that this resistivity decrease was caused by the occurrence of superconductivity in some part of

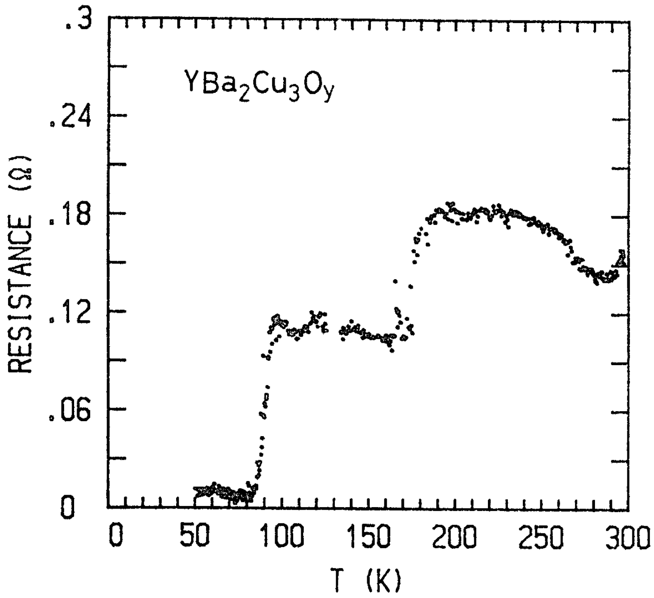


Fig. 3. Temperature dependence of the resistance for a $YBa_2Cu_3O_y$ sample which was sintered in selenium gas and re-annealed at 950 °C in air.

the sample. Unfortunately, the phenomenon disappeared in measurements during the warming cycle.

(2) $(Y_{0.6}Ba_{0.4})_2CuO_y$, $(Y_{0.6}Ba_{0.4})_2Cu_{0.9}O_y$

The samples with these compositions were multi-phase and exhibited the superconducting transition in the 90 K range.

Figure 4 represents the resistivity vs temperature curve for $(Y_{0.6}Ba_{0.4})_2Cu_{0.9}O_y$. The ten-percent deficiency of Cu ions does not give a strong effect on

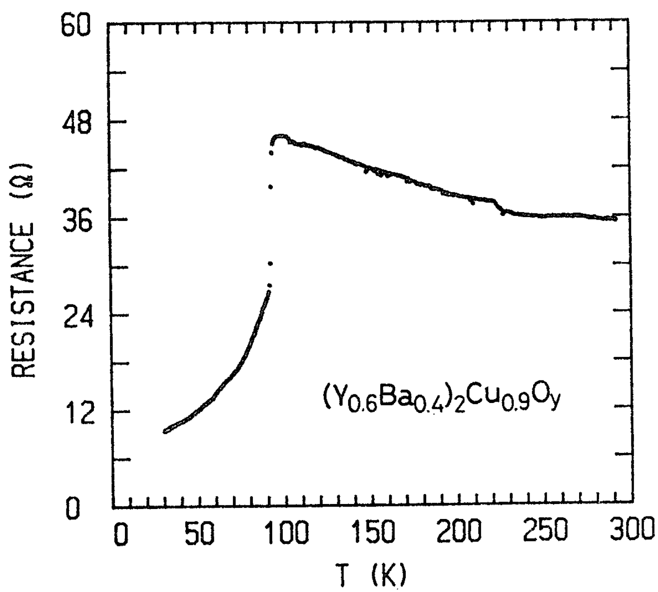


Fig. 4. Temperature dependence of the resistance for a $(Y_{0.6}Ba_{0.4})_2Cu_{0.9}O_y$ sample.

the superconducting transition temperature. The long tail of the curve below 90 K is attributed to the co-existence of the superconducting and normal phase.

(3) $(Y_{0.6}Ba_{0.4})_2Cu_{0.9}Ni_{0.1}O_y$, $(Y_{0.6}Ba_{0.4})_2Cu_{0.9}Zn_{0.1}O_y$

The copper ions were partly substituted with Ni or Zn ions which are the neighboring elements in the periodic table. Figure 5 shows the temperature dependence of the resistivity for $(Y_{0.6}Ba_{0.4})_2Cu_{0.9}Ni_{0.1}O_y$, and Fig. 6 shows the temperature dependence of the resistivity for $(Y_{0.6}Ba_{0.4})_2Cu_{0.9}Zn_{0.1}O_y$. As

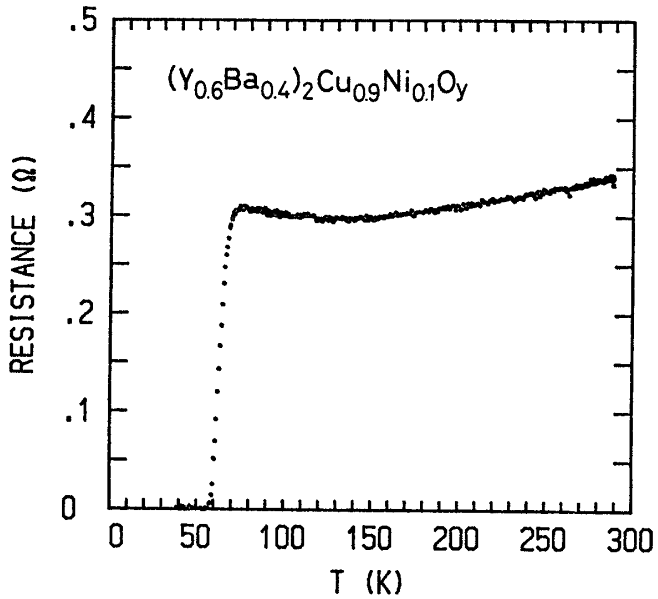


Fig. 5. Temperature dependence of the resistance for a $(Y_{0.6}Ba_{0.4})_2Cu_{0.9}Ni_{0.1}O_y$ sample.

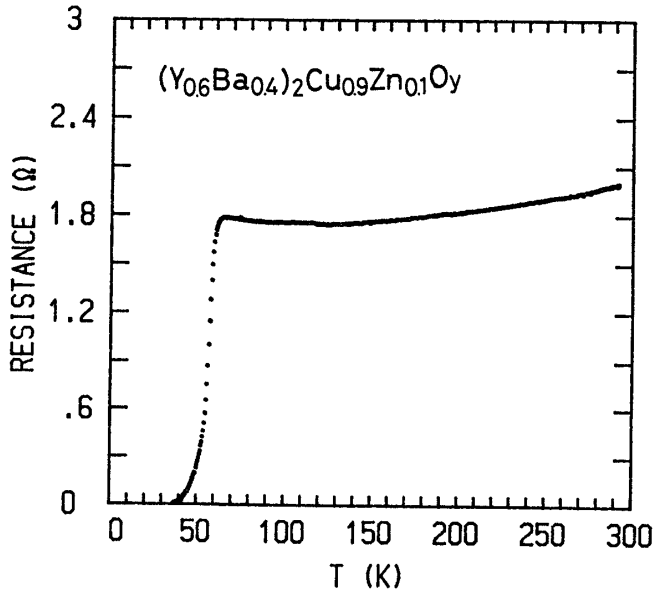


Fig. 6. Temperature dependence of the resistance for a $(Y_{0.6}Ba_{0.4})_2Cu_{0.9}Zn_{0.1}O_y$ sample.

shown in Figs. 5 and 6, only ten percent of Ni or Zn in place of Cu strongly lowers the superconducting transition temperature. Moreover, the effect of Zn substitution is stronger than the Ni substitution. This result demonstrates that the copper ions play an important role in the mechanism of the high-T_c superconductivity.

(4) $Y_{0.7}Sc_{0.3}Ba_2Cu_3O_y$, $Y_{0.7}Cs_{0.3}Ba_2Cu_3O_y$

It was observed that the resistivity of $Y_{0.7}Sc_{0.3}Ba_2Cu_3O_y$ is much smaller compared with the other compounds. Nevertheless, the transition temperature was not raised so much beyond the 90 K range. The single phase in the $Y_{0.7}Sc_{0.3}Ba_2Cu_3O_y$ sample, which was confirmed by X-ray diffraction measurements, shows that Y atoms were actually replaced by Sc atoms.

The Cs substitution for Y did not change T_c compared with $YBa_2Cu_3O_y$.

(5) $YBa_2(CuO_{1-x}S_x)_3O_y$: $x=0.1$, $YBa_2(CuO_{1-x}F_x)_3O_y$: $x=0.1$, 0.3, $YBa_2(CuO_{1-x}Cl_x)_3O_y$: $x=0.1$, 0.3

The sulfur is the element in the same column as oxygen in the periodic table. The superconducting transition in $YBa_2(CuO_{0.9}S_{0.1})_3O_y$ appears at nearly the same temperature as in $YBa_2Cu_3O_y$.

Ovshinsky et al.[11] reported a transition to a zero-resistance state at 155 K in $YBa_2Cu_3F_2O_y$ samples. They suggested that fluorine, which is the neighboring element in the periodic table, may significantly affect the electronic and structural properties in multi-elemental materials. We have also tried to prepare samples which contained F or Cl. However, the increase of T_c was not observed both in the $YBa_2(CuO_{0.9}F_{0.1})_3O_y$ and in $YBa_2(CuO_{0.7}F_{0.3})_3O_y$ samples. The phenomena such as reported by Ovshinsky et al. have not been reproduced in investigations by other workers.

All the samples containing Cl were insulators: $YBa_2(CuO_{0.9}Cl_{0.1})_3O_y$, $YBa_2(CuO_{0.7}Cl_{0.3})_3O_y$, $YBa_2CaCu_3Cl_2O_y$ or $YBa_2Cu_3Cl_2O_y$.

(6) $YSr_2Cu_3O_y$, $YSr_2Cu_3F_xO_y$: $x=0.2$, 0.6, 1, 2

We found that these compounds show semiconducting or insulating behavior. A similar result was reported;[12] $YSr_2Cu_3O_y$ samples obtained only by sintering in oxygen or in air did not exhibit superconductivity down to 4.2 K and superconductivity was observed near 82 K only when they were sintered in argon gas at 1080 °C before annealing in oxygen gas at 880 °C.

SUMMARY

Various compounds, which were derived from the Y-Ba-Cu-O system,

were prepared by solid-state reaction method and the effect of chemical substituents on the superconducting transition was studied by resistivity measurements.

The partial replacement of Y by Sc or Cs gave no effect on the superconducting transition temperature. However, we found that the substitution by Sc makes the room-temperature resistivity greatly decrease.

The Ni or Zn substitution for Cu brought about a strong decrease of the transition temperature. This result shows that the copper ions play an essential role in the occurrence of high-T_c superconductivity.

In the Y-Ba-Cu-O-F or Y-Ba-Cu-O-Cl system, no resistivity drop was observed at higher temperatures than the 90 K range in contrast to the report by Ovshinsky et al.

It was found that the superconducting transition becomes extremely sharp when $YBa_2Cu_3O_y$ samples are sintered in iodine gas and then re-annealed in air or flowing oxygen. This phenomenon was attributed to the removal of inhomogeneous materials between superconducting grains.

Metallic conductivity was not observed in the Y-Sr-Cu-O and Y-Sr-Cu-O-F system.

A sudden decrease of the resistivity was observed around 180 K in a $YBa_2Cu_3O_y$ sample which was re-annealed in flowing oxygen gas after sintering in selenium gas. It appears that this abrupt decrease was induced of a superconducting transition in some part of the sample.

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