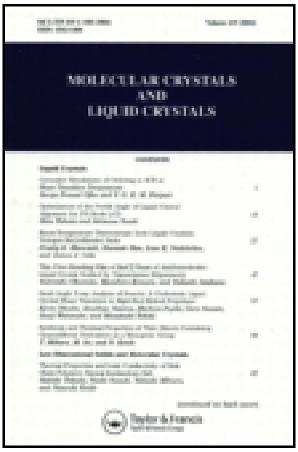

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CRYSTAL STRUCTURE AND SUPERCONDUCTIVITY OF $YBa_2(Cu_{1-x}Fe_x)_3O_y$ PREPARED BY VARIOUS HEAT TREATMENTS

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Abstract $YBa_2(Cu_{1-x}Fe_x)_3O_y$ ($0 \leq x \leq 0.20$) was prepared by three kinds of heat treatments. The crystal structure and superconducting properties of the samples were examined by X-ray powder diffraction, TG and electrical resistivity measurements. The region of orthorhombic phase and superconducting properties strongly depend on the thermal treatments. The results were discussed from the standpoint of Fe distribution.

INTRODUCTION

The effect of substitution for Cu in $YBa_2Cu_3O_y$ by such foreign atoms as Fe, Co, Ni and Zn has been studied by many workers, to investigate the origin of its superconductivity.[1] As the results, such substitution reduces the superconducting transition temperature, Tc, and the substitution by Fe and Co induces the structural phase transition from the orthorhombic to tetragonal. This impurity-induced tetragonal phase differs in nature from the oxygen-disordered tetragonal phase which is realized in undoped $YBa_2Cu_3O_y$ above 650°C in air. The former has high oxygen content ($y \geq 7$) and the latter is oxygen-deficient ($y < 6.5$) one. On the other hand, Ni and Zn do not induce such a phase transition. These behaviors seem to be closely related to the distribution of the substituents in the crystal.

In this paper, we report the experimental results of

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the effect of various heat treatments on the crystal structure and superconducting properties of $YBa_2(Cu_{1-x}Fe_x)_3O_y$, and also discuss the results from the standpoint of Fe distribution.

EXPERIMENTAL

The starting compounds of $YBa_2(Cu_{1-x}Fe_x)_3O_y$ ($0 \leq x \leq 0.20$) were prepared by the solid state reaction of 4N-Y_2O_3, $BaCO_3$, CuO and α-Fe_2O_3 at 900 °C in air. And then the products were divided into some parts and were offered to the three kinds of heat treatments. The first group of the samples (we denote $[O]_s$) was fabricated by an ordinary oxidation process (slow cooling from 850 °C to room temperature in flowing O_2 gas). The second group ($[QO]_s$) was quenched into liq. N_2 from 930 °C in air and then annealed below 400 °C in flowing O_2 gas for more than 20h. The third group ($[NO]_s$) was heated in flowing N_2 gas at 800 °C for 20h followed by slowly cooled to room temperature and then annealed below 400 °C in flowing O_2 gas. The phase identification of these samples was made by the powder X-ray diffraction. The TG (thermogravimetry) measurement was done in air using the pellet-formed samples with 8 mm diameter and 1mm thickness. The super-

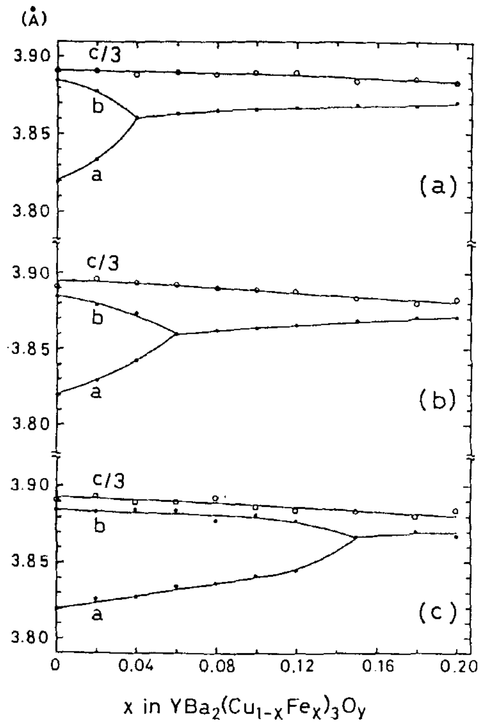

FIGURE 1. Lattice parameters vs. x curves for $YBa_2(Cu_{1-x}Fe_x)_3O_y$. (a)$[O]_s$, (b)$[QO]_s$ and (c)$[NO]_s$.

conducting properties of the samples were investigated by electrical resistivity measurement.

RESULTS AND DISCUSSION

Figure 1(a), (b) and (c) shows the lattice parameters vs. x in $YBa_2(Cu_{1-x}Fe_x)_3O_y$ for $[O]_s$, $[QO]_s$ and $[NO]_s$, respectively. The orthorhombic-to-tetragonal phase transition for $[O]_s$ takes place at about x=0.04 in agreement with the results of many other works.[1] $[QO]_s$ has a somewhat extended orthorhombic region ($0 \leq x < 0.06$) and $[NO]_s$ does much wider orthorhombic region ($0 \leq x < 0.15$). We failed to obtain single phase beyond x=0.18 in all heat treatments.

It is reported that the TG curves for pure $YBa_2Cu_3O_y$ showed a distinct change at about 650 °C in air, which corresponds to the transition temperature from the orthorhombic to oxygen-deficient tetragonal structure.[2] The TG curves for $[O]_s$ with x=0.02, which had orthorhombic structure at room temperature, showed a distinct change at about 630 °C both on heating and cooling at the rate of 10 °C/min. The tetragonal $[O]_s$ with higher iron content than x=0.04 did not show such an anomaly. $[NO]_s$ with the iron content from x=0.02 to 0.12, which had orthorhombic structure at room temperature, showed an

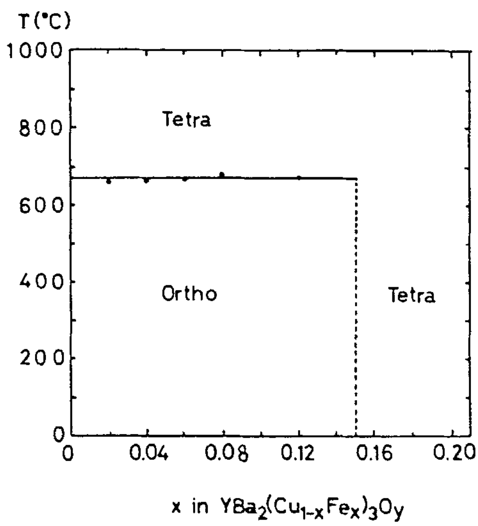

FIGURE 2. Phase diagram of $YBa_2(Cu_{1-x}Fe_x)_3O_y$ for $[NO]_s$. The solid circles show the transition point from the orthorhombic to oxigen-deficient tetragonal structure determined by TG (see text).

anomaly at about 670 °C independent of x in air on heating. The transition temperatures determined by TG measurement are shown in Fig. 2. However, after heating above 900 °C the anomaly was not observed on cooling and the cooled samples had the impurity-induced tetragonal structure, except for the sample with x=0.02. This indicates that the orthorhombic region of the samples strongly depends on the process of the heat treatments.

The x dependence of Tc, together with transition width, ΔTc, determined by the resistivity measurement is shown in Fig. 3(a), (b) and (c) for each $[O]_s$, $[QO]_s$ and $[NO]_s$. In the figure, the closed circles show the midpoint of transition, and the top and bottom of the bars correspond to the temperature with 90% and 10% values of the normal state resistivity. Tc for $[O]_s$ and $[QO]_s$ decreases monotonously with an increase of x. On the other hand, Tc^{onset} for $[NO]_s$ is about 85K independent of x and ΔTc becomes larger with x. The order of Tc at a fixed iron concentration x is $Tc([NO]_s) > Tc([O]_s) > Tc([QO]_s)$.

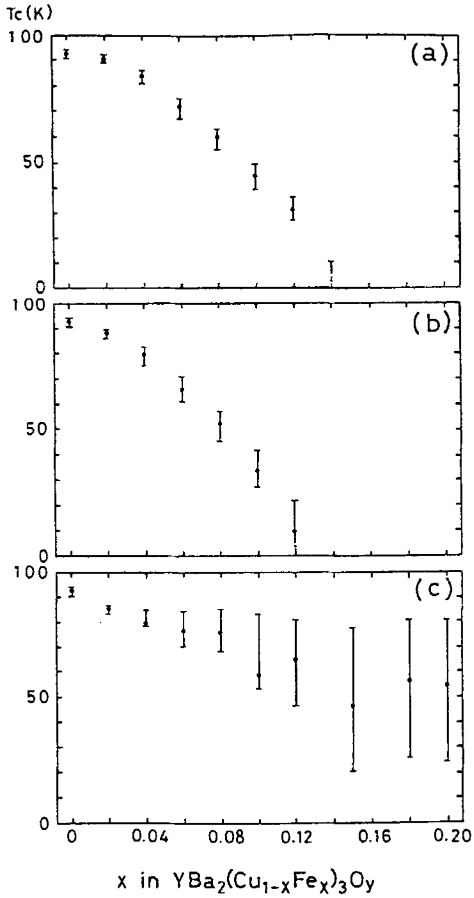

FIGURE 3. Concentration dependence of Tc for (a)$[O]_s$, (b)$[QO]_s$ and $[NO]_s$.

From the above result and the result of our recent study of ^{57}Fe Mössbauer spectroscopy,[3] we have concluded that the clustering of Fe ions in the Cu1-O planes under the lower oxygen fugacity atmosphere is prevalent for the large extension of the orthorhombic region in $[NO]_s$, while the Fe ions are distributed at random in the Cu1-O planes in $[O]_s$ and $[QO]_s$. The size of the orthorhombic domain in $[NO]_s$ is much larger than in $[O]_s$ and $[QO]_s$. The result of Mössbauer measurement also indicates that Fe ions occupy both two Cu sites, and the concentration of Fe substituted for the Cu2 site increases with a decrease of oxygen atmosphere and an increase of temperature during the heat treatment, i.e., $[NO]_s$ has the highest concentration of Fe ions in the $Cu2-O_2$ planes among three kinds of samples, and $[QO]_s$ follows $[NO]_s$. These results suggest that the magnetic pair-breaking effect for this compound is much less important than for traditional superconductors, and 1-D chain structure or orthorhombic domain size is much important on the superconductivity of this compound.

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