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Effect of samarium and lanthanum substitution on the stability of superconductive properties of $YBa_2Cu_3O_x$

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The effect of annealing conditions and solute substitution of samarium and lanthanum on the oxygen deficiency and superconductive properties of $YBa_2Cu_3O_x$-based compounds has been examined. The oxygen deficiency which occurs in samples cooled in air from temperatures above about 400 °C gives poor superconductivity. Although the oxygen content did not change in the samples cooled in a furnace, a degradation of superconductivity, which may be responsible for the formation of lattice imperfections including incipient twin-like bands, was noticed. A partial replacement of yttrium by samarium is found to be effective for stabilizing the superconductivity.

1. Introduction

Since the first discovery of a high-T_c oxide superconductor by Bednorz and Muller [1], a large number of reports on the controlling factors of superconductive properties have accumulated. The appearance of a tetragonal phase in an orthorhombic phase and/or an oxygen deficiency during heating are well known to give poor superconductivity of $YBa_2Cu_3O_x$ compounds [2, 3]. Even when $YBa_2Cu_3O_x$ is slowly cooled from temperatures below that of the phase transformation, giving no change of the orthorhombic structure and the oxygen content, a degradation of superconductive properties has been observed. In a previous paper the degradation of the superconductivity in reheated samples was explained by the effect of the formation of numerous lattice imperfections including new imperfect twin-like bands during reheating [4]. The formation of lattice imperfections and the stability of superconductivity of $YBa_2Cu_3O_x$-based compounds may be sensitive to the partial replacement of yttrium by other lanthanides.

In this paper, part of the yttrium is replaced by other lanthanides with a larger ion radius such as samarium and lanthanum, and then the effect of annealing conditions and solute substitution on the oxygen deficiency and the superconductive properties has been examined.

2. Experimental details

$YBa_2Cu_3O_x$, $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$ and $(Y_{0.95}La_{0.05})Ba_2Cu_3O_x$ oxide samples were prepared from mixed powders of the corresponding proportions of Y_2O_3, $BaCO_3$, CuO, Sm_2O_3 and La_2O_3. The pellet was ground and formed into a bar-shaped specimen (2 mm × 5 mm × 20 mm) after pre-sintering at 950 °C for 12 h, sintered again at 950 °C for 24 h in air and then slowly cooled to room temperature in a furnace. Samples in this state, hereafter called virgin samples, were again annealed at various temperatures for 1 h and then cooled in the same furnace or cooled in air at rates of about 90 °C h^{-1} or 13 °C sec^{-1}, respectively.

The electrical resistivity was measured by a conventional d.c. four-probe method with a current of 10 mA, using indium contacts soldered by an ultrasonic soldering technique. The resistance was also measured as a function of temperature in a fixed magnetic field. The oxygen content was estimated by measuring the weight change after annealing. The oxygen deficiency during annealing was also confirmed by thermogravimetric analysis and the phase transformation was examined by differential scanning calorimetry analysis. The crystal structure of the products at selected temperatures was examined by powder X-ray diffraction.

3. Results and discussion

Virgin samples cooled in the furnace showed a sharp superconductive transition in the resistivity curves, and the offset (zero-resistance state) temperatures of $YBa_2Cu_3O_x$, $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$ and $(Y_{0.95}La_{0.05})Ba_2Cu_3O_x$ were 93.1, 90.7 and 88.3 K, respectively. In this paper the transition temperature is hereafter evaluated by the offset temperature, T_c. A marked change in the resistivity curves was observed in samples cooled in air after reheating: T_c decreased and the transition became broader with an increment of the quenching temperature and cooling rate. The degradation of superconductivity in the samples

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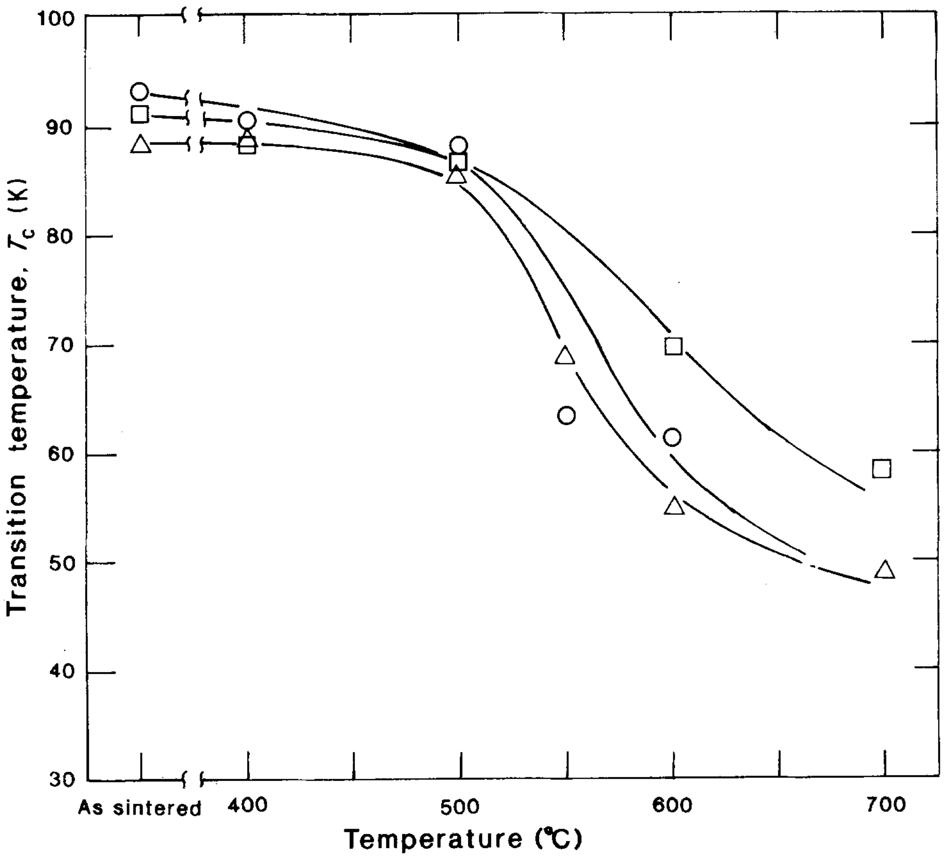

Figure 1 Transition temperature T_c as a function of annealing temperature. The samples were cooled in air from the indicated temperatures after annealing for 1 h. (○) $YBa_2Cu_3O_x$, (□) $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$, (△) $(Y_{0.95}La_{0.05})Ba_2Cu_3O_x$.

cooled in air is represented in Fig. 1 as the change of T_c. According to differential scanning calorimetry analysis, the phase transformation of $YBa_2Cu_3O_x$, $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$ and $(Y_{0.95}La_{0.05})Ba_2Cu_3O_x$ from the orthorhombic to the tetragonal phase during heating at a rate of 10 °C min^{-1} occurs at 658, 656 and 658 °C, respectively. The marked degradation of T_c in the samples cooled in air from temperatures above that of the phase transformation is naturally responsible for the appearance of the tetragonal phase in the orthorhombic phase. T_c decreases slowly with increasing annealing temperature up to 400 °C, followed by a sharp decrease above 500 °C. Samarium substitution is found to stabilize the superconductivity against heat treatment. In this temperature range below 600 °C only the orthorhombic phase was confirmed to remain in three compounds by X-ray analysis.

The weight change due to oxygen absorption and desorption during cooling and heating occurs in the temperature range above about 450 °C as shown in Fig. 2. If the heating and cooling is performed slowly enough, the desorbed oxygen sites formed during heating should be fully filled again by oxygen atoms during cooling. The broad transition in the resistivity and the decrease of T_c in samples cooled in air from temperatures below that of the phase transformation are mainly due to oxygen deficiency; this is supported by the weight loss measurements after cooling as shown in Fig. 3. The appearance of oxygen vacancies in the orthorhombic phase leads to a change of the lattice parameters and a significant degradation of superconductivity. The difference between lattice parameters *a* and *b* in these compounds decreased with increasing oxygen vacancies in the orthorhombic crystal, and finally the transformation to the tetragonal structure was accomplished at a weight loss of more than about 1%.

Fig. 4 shows the variation of T_c of these compounds with the weight loss. The oxygen deficiency gives the instability of the orthorhombic structure against the tetragonal structure, and then T_c decreases almost in proportion to the weight loss. In this case, samarium substitution also has an advantage in the stability of superconductivity. On the other hand, weight loss cannot be observed between the virgin sample and the sample cooled in the same furnace after reheating for 1 h at temperatures between 300 and 800 °C as shown in Fig. 3. This is reasonable since the total amount of oxygen which is desorbed during reheating must again be absorbed in a similar cooling process.

The superconductive properties of samples cooled in the same furnace after reheating at selected temperatures, however, differ from those of their virgin samples as shown in Fig. 5. The resistivity curve did not change significantly by cooling in the furnace after reheating up to 400 °C, while T_c decreased for samples annealed in the temperature range between 500 and 600 °C where the orthorhombic structure was still stable. When $YBa_2Cu_3O_x$ is annealed above 700 °C, the resistivity curve almost overlaps that of the virgin sample. This is not surprising since the phase transformation from the tetragonal to the orthorhombic structure and also the oxygen absorption occur again perfectly in a similar cooling process. The degradation

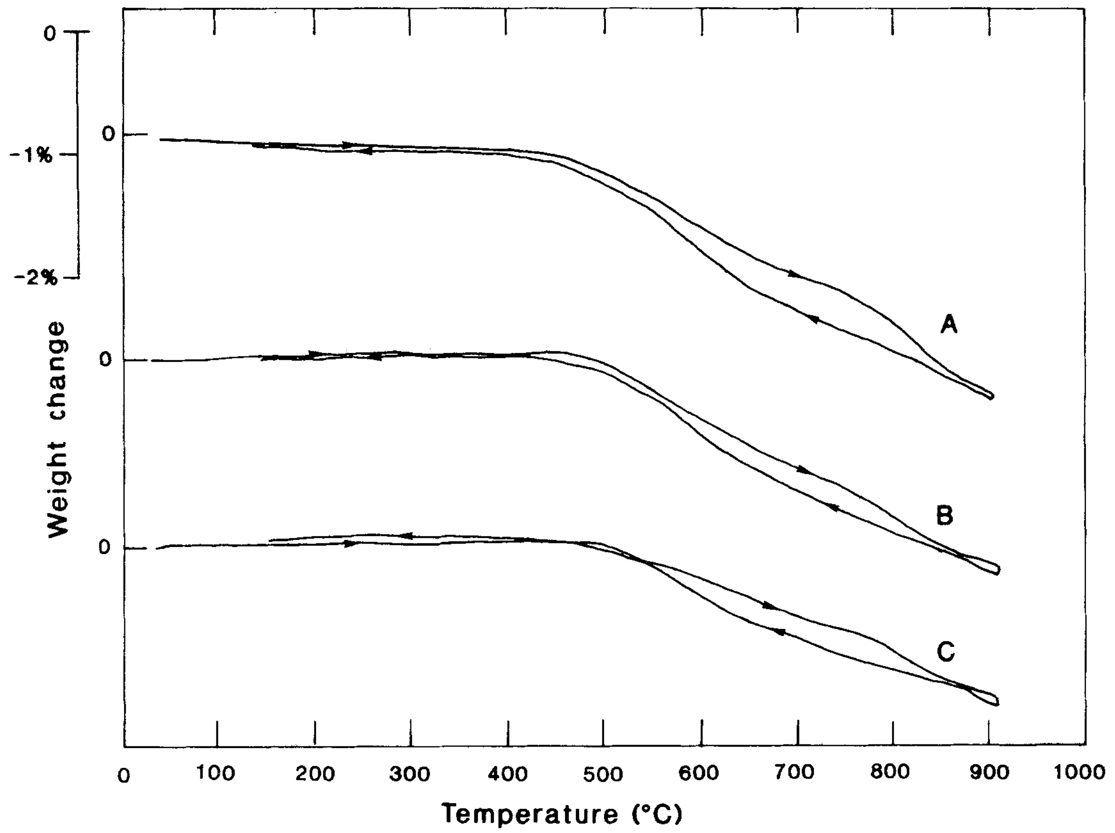

Figure 2 Weight change during heating and cooling by thermogravimetric analysis. The heating and cooling were carried out at a rate of 10 °C min^{-1}. (A) $YBa_2Cu_3O_x$, (B) $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$, (C) $(Y_{0.95}La_{0.05})Ba_2Cu_3O_x$.

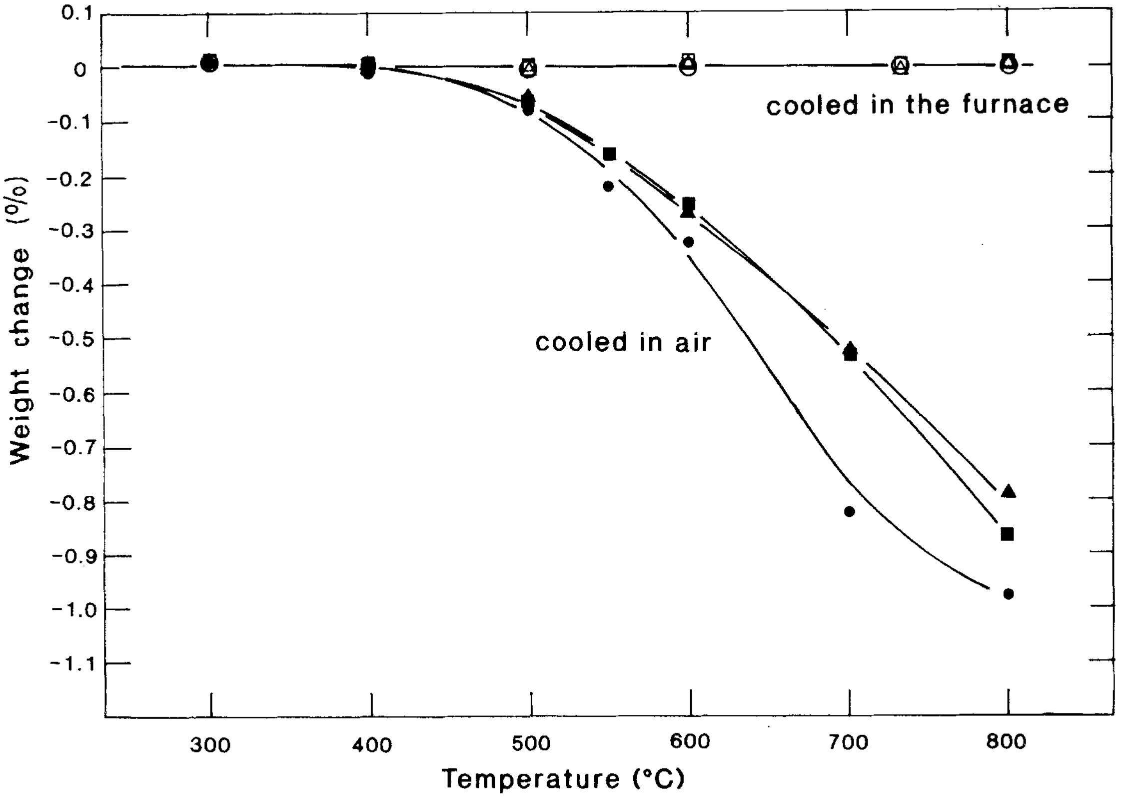

Figure 3 Weight change as a function of the annealing temperature. The samples were cooled from various temperatures after annealing for 1 h. Samples cooled in the furnace: (○) $YBa_2Cu_3O_x$, (△) $(Y_{0.95}Sm_{0.05})$ $Ba_2Cu_3O_x$, (□) $(Y_{0.95}La_{0.05})Ba_2Cu_3O_x$. Samples cooled in air: (●) $YBa_2Cu_3O_x$, (▲) $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$, (■) $(Y_{0.95}La_{0.05})Ba_2Cu_3O_x$.

of superconductivity in the samples annealed at the intermediate temperature cannot be interpreted by an oxygen deficiency and/or the existence of the tetragonal phase.

The effect of annealing on the degradation of superconductivity is remarkably noticeable in the resistivity change in an applied magnetic field as shown in Fig. 6. The transition of the resistivity becomes significantly

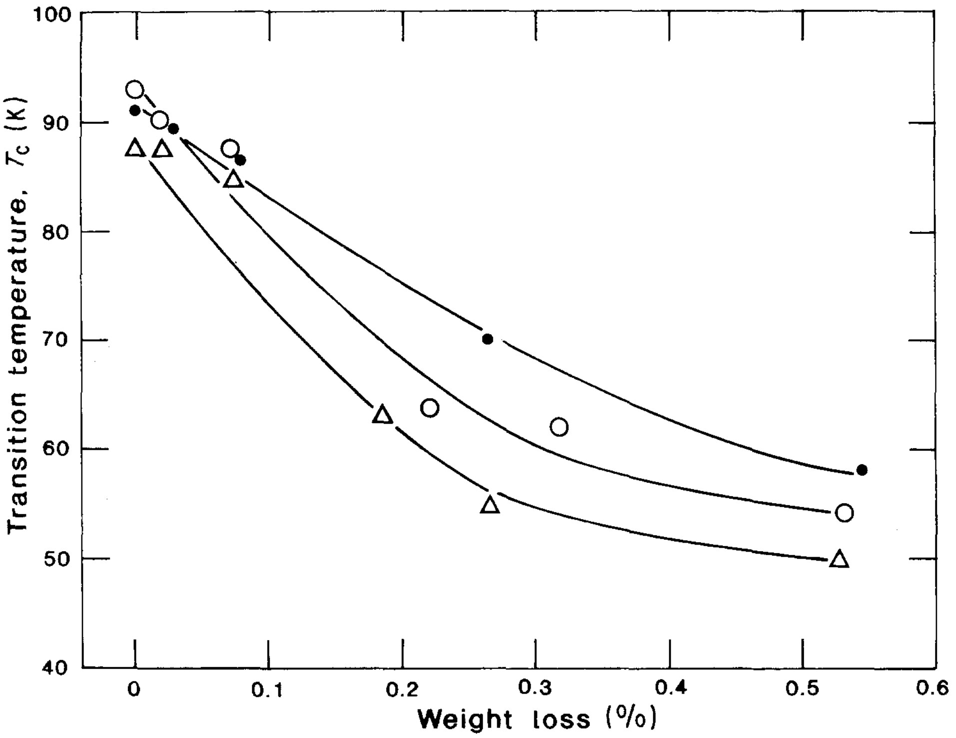

Figure 4 Variation of the transition temperature with weight loss. (●) $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$, (○) $YBa_2Cu_3O_x$, (△) $(Y_{0.95}La_{0.05})Ba_2Cu_3O_x$.

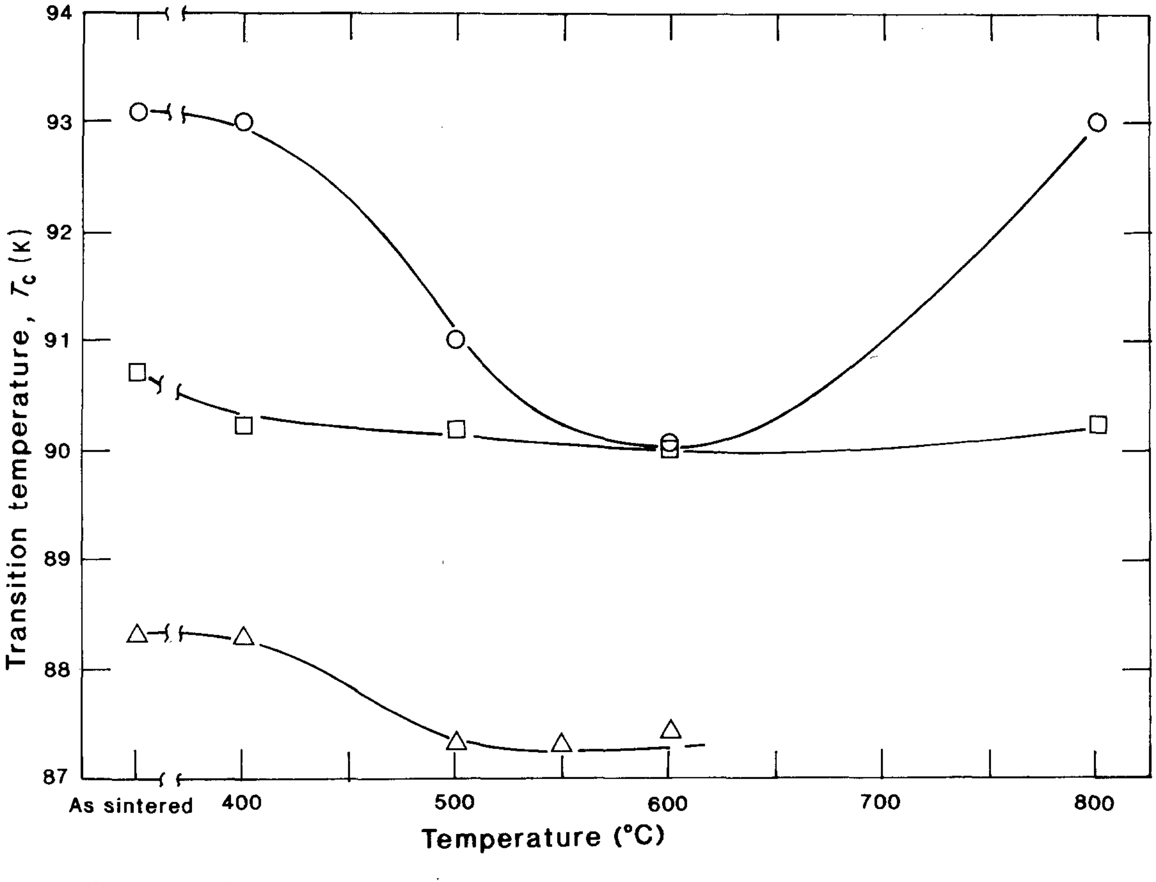

Figure 5 Variation of T_c with the annealing temperature. The samples were cooled in the furnace after annealing at the indicated temperatures for 1 h. (○) $YBa_2Cu_3O_x$, (□) $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$, (△) $(Y_{0.95}La_{0.05})Ba_2Cu_3O_x$.

broader with increasing applied magnetic field. This suggests the formation of a low-H_{c2} phase which gives a weak link in the superconductivity.

The temperature dependence of H_{c2} defined by a zero-resistance state is given in Fig. 7, together with the result for the virgin sample. The negative slope of the H_{c2}–T curves rapidly decreases with decreasing temperature and finally seems to be linear. Using the well-known formula $H_{c2}(0) = -0.69\ (dH_{c2}/dT)_{T_c}$ [5] for estimation, the values of $H_{c2}(0)$ at 0 K for the virgin and reheated $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$ were 73 and 54 T, respectively.

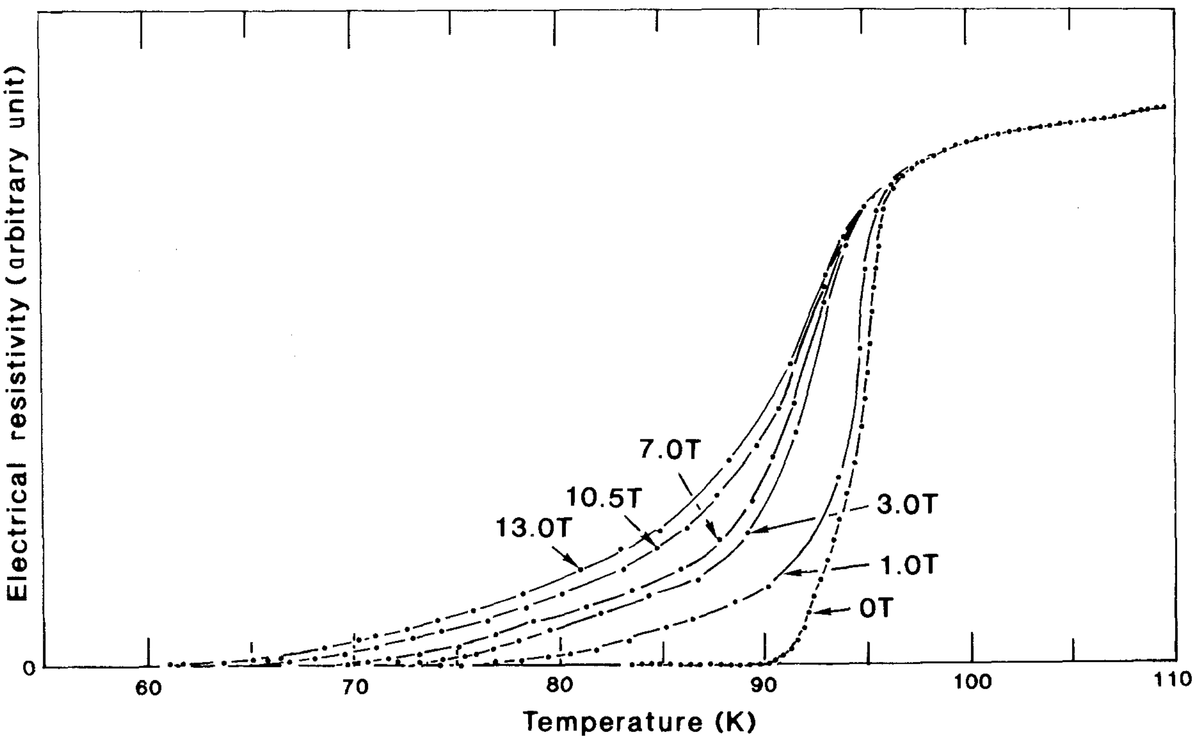

Figure 6 Temperature dependence of the resistivity of $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$ cooled in the furnace after annealing at 400 °C for 1 h in various magnetic fields.

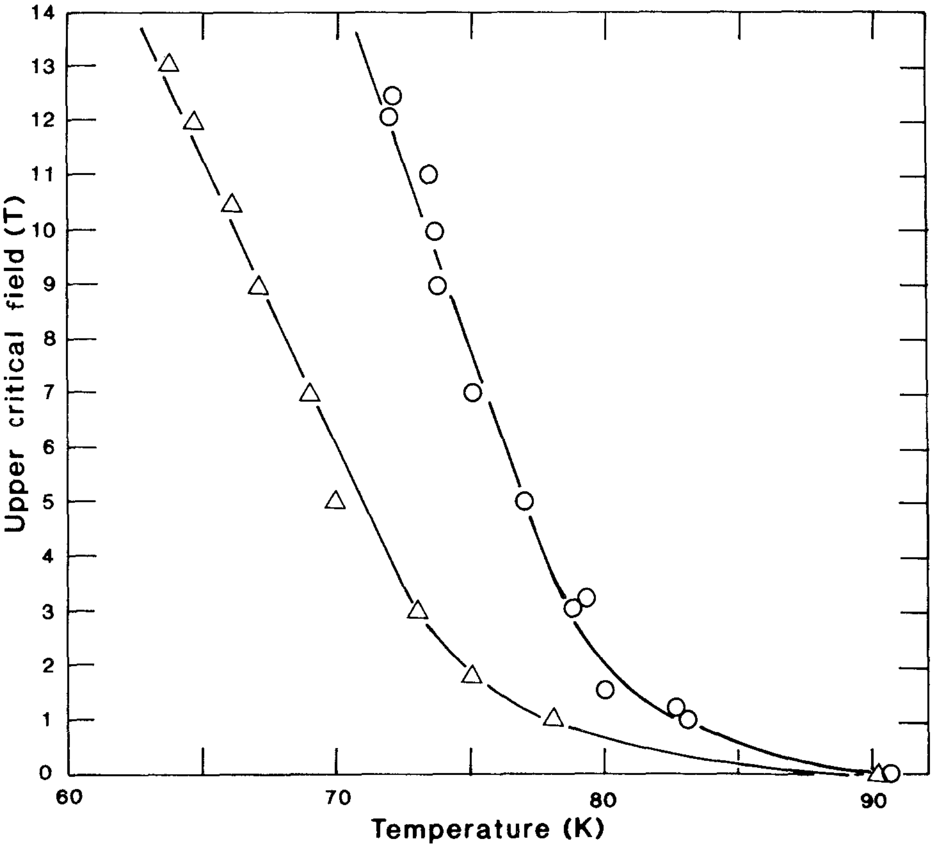

Figure 7 Temperature dependence of the upper critical magnetic field of $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$. (○) Virgin sample, (△) sample cooled in the furnace after annealing at 400 °C for 1 h.

The weak link in superconductivity is in general given by grain boundary segregation and/or lattice imperfections at the boundaries [6, 7]. When $YBa_2Cu_3O_x$ is reheated at temperatures below 650 °C, new imperfect twin-like bands which contain a large local strain may be introduced into as-grown twin lamellae as reported by Iijima *et al.* [8]. As oxygen atoms go in and out of the oxide compounds during cooling and heating, lattice defects such as vacancies, dislocations and stacking faults, which would be concentrated at the grain and/or twin boundaries, may also be induced during cooling since the oxygen atoms cannot necessarily occupy the same sites. It is easily imaginable that such lattice defects (including imperfect twin-like bands) give poor conductivity. In fact a degradation of superconductive properties due to lattice defects has been observed in $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$ [9] and $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ compounds [10] when numerous lattice defects are produced at grain and/or twin boundaries by the shock waves generated by irradiation by a high-powered short-pulsed laser.

The degradation of superconductivity due to induced lattice defects can be suppressed by the partial replacement of yttrium by solute substitution of samarium (see Fig. 5). The formation of incipient twin-like bands may be responsible for the local strains induced by lattice mismatch between the tetragonal and orthorhombic structures. The ion radius of the lanthanides should contribute to the formation of lattice defects during annealing, but the stability of superconductivity of compounds containing different lanthanides is not directly related to the ion radii of the lanthanides because of their ion radius being ordered in the sequence of La > Sm > Y.

4. Conclusions

1. The oxygen deficiency which occurs on cooling in air from temperatures above about 400 °C gives poor superconductivity of $YBa_2Cu_3O_x$, $(Y_{0.95}Sm_{0.05})Ba_2Cu_3O_x$ and $(Y_{0.95}La_{0.05})Ba_2Cu_3O_x$.

2. Even in the case of being slowly cooled in the furnace, T_c decreases with increasing annealing temperature. The degradation of superconductivity may be responsible for the formation of lattice imperfections including incipient twin-like bands.

3. A partial replacement of yttrium by samarium is effective for suppressing the degradation of superconductivity due to lattice defects.

4. The degradation of superconductivity by reheating and then cooling is mostly found in a decrease of H_{c2}. The broad transition in the resistivity under an applied magnetic field suggests the presence of a low-H_{c2} phase.

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