Effect of annealing on the superconductivity of $Bi_2Sr_2CaCu_2O_y$ single crystals

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High-quality as-grown $Bi_2Sr_2CaCu_2O_y$ single crystals with superconducting transition temperatures T_c of 70–83 K have been annealed in air, flowing oxygen, and nitrogen at 400–750 °C. ac susceptibility measurements show that at 450–550 °C T_c is atmosphere and time independently enhanced to 85–86 K and a very narrow diamagnetic transition ΔT_c (10–90 % of the complete transition) of 0.5–1 K is obtained, and at 550–750 °C when treated in nitrogen or oxygen T_c increases or decreases and ΔT_c broadens with annealing temperature compared with crystals annealed at 450–550 °C. The results are difficult to explain simply by the consideration of oxygen diffusion. Combined with the phase decomposition induced in the annealed crystals, it is suggested that the structural modification may play an important role in the variation of superconductivity of $Bi_2Sr_2CaCu_2O_y$ superconductors.

INTRODUCTION

It has been reported that T_c of $Bi_2Sr_2CaCu_2O_y$ (Bi-2:2:1:2) superconductors can be shifted over a range of at least 15 K (Refs. 1,2) and up to 96 K (Ref. 3) by proper thermal treatments. Clarification of this variation of T_c is undoubtedly important for understanding the mechanism of high-T_c superconductivity and also for materials design. For this purpose, recently a great deal of effort has been devoted to the study of the effect of annealing on the superconducting properties of the $Bi_2Sr_2CaCu_2O_y$ system.

For the polycrystalline $Bi_2Sr_2CaCu_2O_y$ superconductor, the effect of annealing on T_c has been studied in detail.[1,3–9] It was concluded that T_c depended strongly on oxygen content and there existed an optimum oxygen concentration corresponding to a maximum T_c in the system,[4,8,9] though the optimum amount was quite different according to different authors.[1,9] At the same time, structural changes associated with the annealing treatments were also suggested to be responsible for the variation of superconductivity by some groups.[5,10]

However, as far as the single crystal $Bi_2Sr_2CaCu_2O_y$ is concerned, T_c of which was found to be more sensitive to oxygen configuration[11] and usually the structural change of which can be easily observed in contrast to that of polycrystalline samples, the effect of annealing on superconductivity has not been studied systematically until now. The relationship between oxygen content and T_c and ΔT_c (10–90 % of complete transition) of the single crystals has been investigated by Mitzi *et al.*[12] and Emmen *et al.*[13] under certain annealing conditions, but some points are still controversial. For example, according to Mitzi *et al.*, ΔT_c was essentially unchanged after the crystal annealed at 540 °C in different oxygen pressure, while Emmen *et al.* reported that very narrow diamagnetic transitions were observed for the crystals treated in 1 bar oxygen pressure and at 400–700 °C. Moreover, the effect of structural changes induced by annealing treatments such as the phase decomposition[14,15] on superconductivity is rarely discussed.

As has been pointed out,[13] T_c and ΔT_c of single crystals are both indications for the distribution of excess oxygen concentration and therefore determine the kinetics of oxygen in and out diffusion. On the other hand, according to Runde *et al.*[16] the kinetics of oxygen diffusion in $Bi_2Sr_2CaCu_2O_y$ single crystals is strongly temperature and time dependent, which should be reflected by the variation of T_c and ΔT_c.

In view of these points, for the single crystal, more extensive studies on the dependence of T_c and ΔT_c on the annealing atmosphere, temperature, and time are needed. In this paper, we report the results of ac susceptibility measurements on a number of high-quality $Bi_2Sr_2CaCu_2O_y$ single-crystal sheets before and after annealing in air, flowing oxygen, and nitrogen at 400–750 °C and for different times. Every crystal sheet was annealed for only one time and some crystal sheets employed were cut up from one large crystal so that more direct and comparative studies on the effect of annealing on superconductivity of $Bi_2Sr_2CaCu_2O_y$ superconductors could be derived. It is found that the results are difficult to explain simply by the oxygen configuration, and we suggest that the structural modification indicated by surface phase decomposition in the annealing processes may play an important role in the variation of superconductivity of $Bi_2Sr_2CaCu_2O_y$ superconductors.

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EXPERIMENT

$Bi_2Sr_2CaCu_2O_y$ single-crystal sheets with thickness around 30 μm and average in-plane dimensions of 7 mm$\times$3 mm were grown from Bi-rich melts by a directional solidification method. The atomic ratio of the grown melts was of 2.4Bi:2.0Sr:1.0Ca:2.0Cu and the thermal cycle program for the crystal growing process was similar to that described elsewhere.[17] To ensure the homogeneity of the crystals with regard to the composition, structure, and oxygen content, bright crystals with in-plane dimensions of 3 mm$\times$2 mm and thicknesses of about 20 μm were chosen as candidates for the annealing experiments. In some cases, large crystal sheets with dimensions around $8\times3\times0.02$ mm^3 were also chosen and then cut up into several pieces by a sharp scalpel to undergo different annealing treatments. Before annealing, all the crystals were characterized by x-ray diffractions (XRD), both the (00*l*) diffraction and the rocking curve of the (0010) main reflection, so that well-oriented single crystals with only the (00*l*) diffractions of the 2:2:1:2 phase were selected. After the ac susceptibility measurements the selected as-grown samples were then loaded in a high-purity alumina boat to undergo thermal treatments. All the treatments were performed in a tubular furnace with temperature and time monitored by a microprocessor, and the gas flow rate was adjustable. Annealing treatments in O_2 or air were followed by furnace cooling in the same atmosphere and thermal treatments in flowing N_2 were completed by quenching to room temperature in the same atmosphere.

ac susceptibility was measured with a magnetic field (0.02 Oe, 108 Hz) perpendicular to the crystal basal plane ($H\|c$). X-ray diffraction data were collected using a rotating-anode diffractometer (D/Max-γA, Rigaku) with graphite monochromatized Cu$K\alpha$ radiation.

RESULTS AND DISCUSSION

Figure 1 shows the variations of the ac susceptibility for a set of single crystals before and after annealing in air at 400, 500, 550, and 750 °C for 20 h. At 400 °C, T_c and ΔT_c of the annealed crystal are almost the same as those of the as-grown crystal. Data on another sample annealed under the same conditions but with T_c as grown lower show that after annealing T_c is slightly increased but ΔT_c remains essentially unchanged (not shown in the figure). For the crystals annealed at 500 and 550 °C, T_c is increased to the same value of almost 86 K and the diamagnetic transition becomes very steep with ΔT_c of about 0.5 K. After annealing at 750 °C, T_c of the crystal is increased to 88 K but ΔT_c is broadened to 2.2 K.

The enhancement of T_c and the very narrow diamagnetic transition are commonly found for the crystals annealed at 450–550 °C. In this temperature range T_c always increases to 85–86 K and ΔT_c decreases to 0.5–1 K, and it is revealed to be time and atmosphere independent. In Fig. 2, for the three single crystals annealed at 550 °C and for different times, whatever the T_c as grown is, T_c is increased to 85 K and for only 1.5 h the diamagnetic transition has dramatically steepened. The narrowness of the diagmagnetic transitions was also observed by Emmen *et al.*[13] for the crystals annealed at temperatures from 450 to 700 °C in 1-bar oxygen but for 60 h so that a homogeneous oxygen content through the entire sample is obtained. In our experiments, however, the sharp transition of the crystals annealed at 450–550 °C is almost time independent. This is difficult to explain in view of the oxygen diffusion and equilibrium, which means that the homogeneity of the superconductive phase of the crystals annealed at 450–550 °C may not be obtained by the homogeneous oxygen content.

In fact, x-ray diffraction patterns of the crystals annealed at temperatures over 450 °C are all changed. Figure 3 shows a group of typical XRD patterns of the crys-

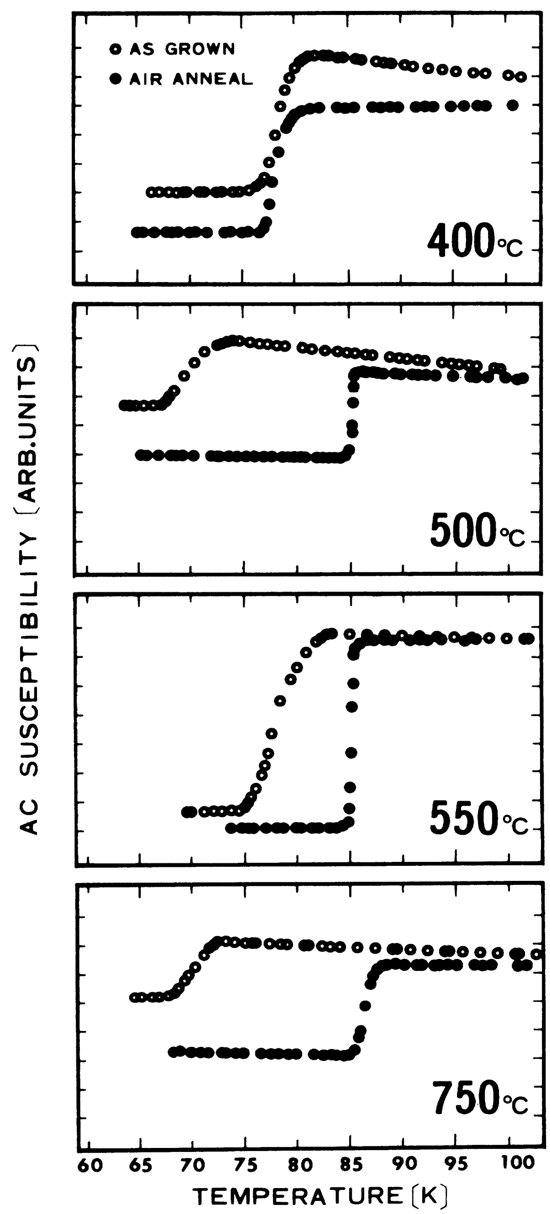

FIG. 1. ac susceptibility variations of the $Bi_2Sr_2CaCu_2O_y$ single crystals as grown and annealed in air at 400, 500, 550, and 750 °C for 20 h.

tals annealed in air at 400, 450, 550, and 650 °C for 20 h. At 400 °C, no reflection other than the (00l) reflections of the $Bi_2Sr_2CaCu_2O_y$ (2:2:1:2) phase (indexed) is observed. But when temperature is increased to 450 °C, phases of Bi_2O_3 (pseudo-orthorhombic symmetry and $a = 5.850$ Å, $b = 8.165$ Å, and $c = 13.827$ Å) with reflections denoted by open squares and $Bi_2O_{2.75}$ (tetragonal, $a = 3.85$ Å and $c = 12.25$ Å) indicated by open circles are segregated from the 2:2:1:2 phase. When annealed at 550 °C, one more phase with reflections at Bragg angles 9.5°, 18.9°, 28.5°, and 35.3° is created which has been frequently observed in the Bi-Sr-Ca-Cu-O compounds[18–20] and is regarded to be associated with a Cu-free $Bi_xSr_yCa_z$ oxide phase with crystal structure similar to the tetragonal $Bi_{1.1}Sr_{0.9}O_{2.55}$, which displays characteristic spacings of 9.3 Å (110).[21] At 650 °C the as-grown crystals have undergone structural changes more dramatically. In addition to the $Bi_xSr_yCa_z$ oxide phase, the $Bi_2Sr_2CuO_y$ (2:2:0:1) phase appears (the reflections are indicated by dots in the top panel in Fig. 3). Studies on the phase determination and evolution have indicated that the decomposed phases are strictly temperature dependent and are found mainly in the surface part of the annealed crystals.[15]

The temperature (around 450 °C) at which the phase decomposition (detected by XRD) of the as-grown $Bi_2Sr_2CaCu_2O_y$ single crystals begins to take place is in accordance with the temperature at which (after the samples were annealed) the very narrow diamagnetic transition can be observed. The phases of Bi oxides decomposed from the as-grown single crystals, though mainly in the surface part of the annealed crystals, provide important information on the stability of the whole crystals. The inset of the top panel in Fig. 2 shows part of the XRD pattern for the annealed crystal, which may reflect that the structure modification in the annealed crystal indicated by the surface-phase decomposition is connected with and thereby responsible for the homogeneity of the superconductive phase of the crystals.

It should be mentioned here that we have removed the surface decomposed part from some annealed crystals by using adhesive tapes to detect whether the variation of superconductivity of the crystal is created by the surface decomposed part or not. ac susceptibility measurements

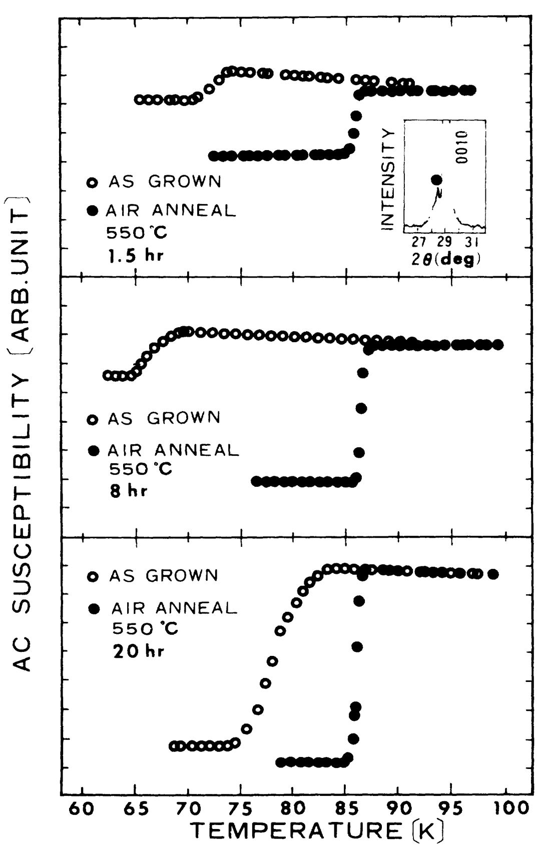

FIG. 2. The temperature dependences of ac susceptibility for three crystals as grown and annealed in air at 550 °C for 1.5, 8, and 20 h. The inset in the top panel shows part of the XRD pattern of the annealed crystal.

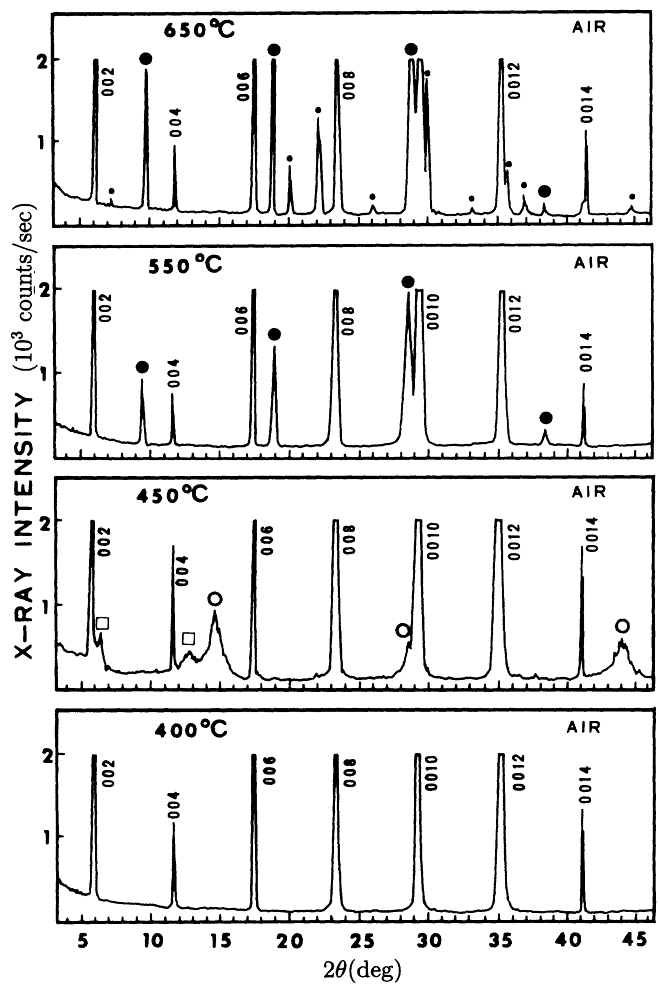

FIG. 3. X-ray-diffraction patterns of $Bi_2Sr_2CaCu_2O_y$ single crystals annealed at 400, 450, 550, and 650 °C for 20 h. Reflections of Bi_2O_3, $Bi_2O_{2.75}$, and $Bi_xSr_yCa_z$ oxide decomposed from the 2:2:1:2 phase (indexed) are represented by open squares, open circles, and full circles, respectively. Reflections denoted by dots in the top panel are assigned to the $Bi_2Sr_2CuO_y$ (2:2:0:1) phase.

on the newly cleaved crystals have shown that the answer is negative. It also confirms that the homogeneity of the superconductive phase of the whole annealed crystals is achieved.

To observe the variations of T_c and ΔT_c of the same crystal annealed in different atmosphere, high-purity and well-oriented $Bi_2Sr_2CaCu_2O_y$ single crystal with large dimensions has been selected and then cut up into two pieces to undergo treatments at the same temperature but in O_2 or N_2, respectively. Figure 4 shows the typical results of ac susceptibility data on two sets of the crystals annealed at 550 and 750 °C and for 20 h. For comparison, results of the as-grown crystals are also shown in the figure. It can be seen that for the crystal annealed in N_2 or O_2, ΔT_c always increases, which is surely difficult to explain in terms of the variation of oxygen configuration. If the variation of T_c is only controlled by the oxygen concentration in the crystals, T_c should shift in opposite directions when treated in the two kinds of atmosphere.[2,22]

On the other hand, in Fig. 4 it is shown that T_c of the crystal sheet treated in N_2 is always higher than that of the sheet treated in O_2. And when the temperature is increased from 550 to 750 °C, T_c of the crystals annealed in nitrogen increases from 87 to 92 K and T_c of the crystals treated in oxygen decreases relatively from 84.5 to 82 K. The diamagnetic transitions of the crystal annealed at 550 °C are steeper than those of the crystals annealed at higher temperatures such as 750 °C. All these facts indicate that the oxygen content and contribution are responsible for the variation of superconductivity of the crystals when treated at higher temperatures (over 550 °C).

The phase situation of the crystals annealed in flowing nitrogen or oxygen were also examined by x-ray diffraction. It is revealed that at 450–550 °C phases decomposed are the same as those from the crystals annealed in air (cf. Fig. 3), and at higher temperature the phase decomposition in O_2 is more dramatic than that in N_2 (Fig. 5). This means that at higher temperature the surface-phase decomposition is related to the annealing atmosphere, but at 450–550 °C it is not.

According to the oxygen tracer diffusion experiments reported by Runde *et al.*,[16] oxygen diffusion in $Bi_2Sr_2CaCu_2O_y$ single crystals is rather slow at temperatures lower than 550 °C (at 500 °C for 216 h, about 1.2 μm in the *c* direction) but increases rapidly with increasing temperature which further confirms that at lower temperature the oxygen mobility in the crystals is too low to achieve oxygen homogeneity of the entire crystal within the annealing time stated. Thus, in view of the experimental results mentioned above and the phases segregat-

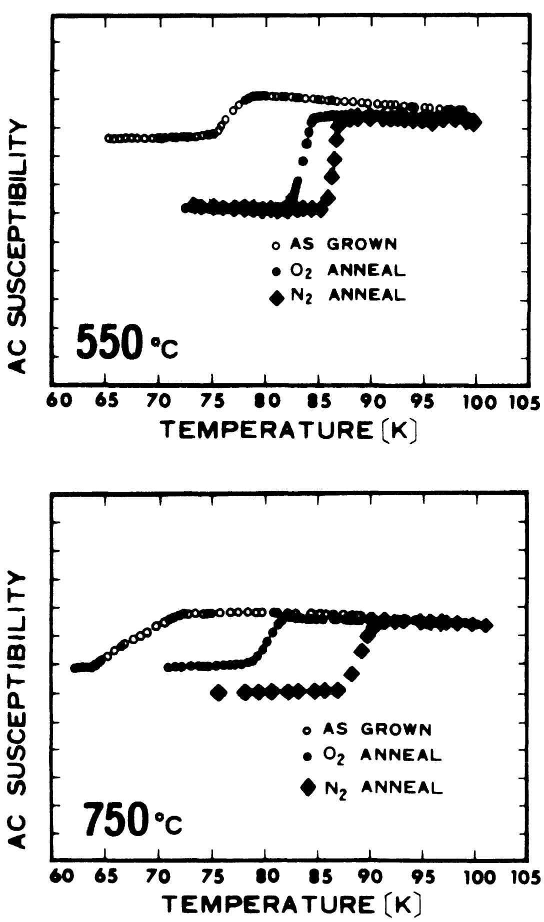

FIG. 4. ac susceptibility data on crystal sheets as grown, O_2 annealed, and N_2 annealed for 20 h at 550 °C and 750 °C, respectively. The crystal sheets annealed at the same temperature are cut from one large crystal.

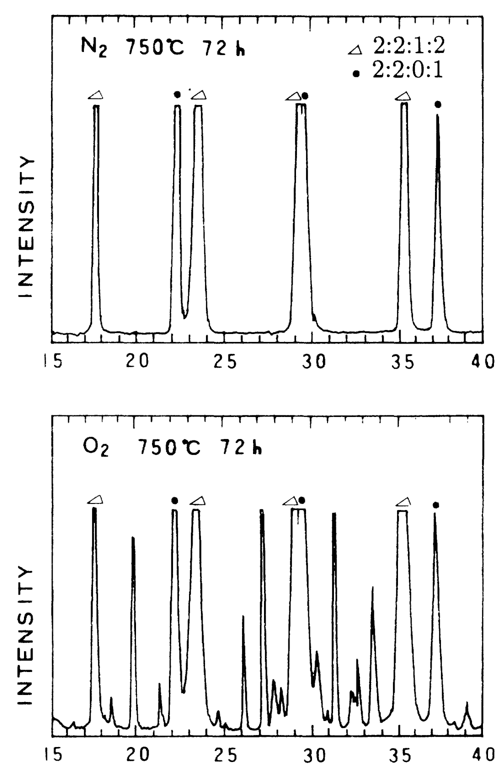

FIG. 5. X-ray-diffraction patterns of $Bi_2Sr_2CaCu_2O_y$ single crystals annealed at 750 °C for 72 h in flowing N_2 and O_2, respectively.

ed (bismuth oxides and bismuth strontium oxides), we suggest that when the annealing temperature is over 450 °C, the structural modification in $Bi_2Sr_2CaCu_2O_y$ single crystals occurs and it is responsible for the variations of superconductivity in the annealed crystals. In general, the process of the structural adjustment should be atmosphere and time independent so that after annealing, even in different atmospheres and for a short time, the superconducting homogeneity of the crystal can be achieved. Further investigations of the structural changes such as the variation in the modulations[3,5] are in progress.

CONCLUSIONS

In summary, a number of high-quality as-grown $Bi_2Sr_2CaCu_2O_y$ single crystals with T_c 70–83 K have been annealed in air, flowing nitrogen, and oxygen at 400–750 °C, and for different times. After being annealed at 450–550 °C all the crystals have shown superconducting transitions at a value around 86 K with ΔT_c of about 0.5 K, which is almost atmosphere and time independent and therefore difficult to explain by consideration of the oxygen configuration. Together with the surface-phase decomposition observed, structure modification in the annealed crystals is suggested to occur and to be responsible for the variation of superconductivity of the crystals. When heat treated at higher temperatures (550–750 °C) and in different atmospheres, temperature dependences of T_c and ΔT_c of the annealed crystals can be well interpreted with the points of the oxygen configuration as well as the structural modification.

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