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Effects of oxygen doping and structural distortion on the superconductivity of $Bi_2Sr_2CaCu_2O_y$ single crystals

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Abstract. Effects of oxygen doping and structural distortion on the superconductivity of $Bi_2Sr_2CaCu_2O_y$ (Bi2212) were studied by ac susceptibility and x-ray diffraction measurements for a group of high-quality single crystals. The crystals were annealed at 600 °C and under different oxygen pressures ranging from 10^{-7} to 6080 Torr. It was found that the *c*-axis length showed a plateau at 10^{-7}–10^{-1} Torr and decreased with increasing oxygen pressure above 10^{-1} Torr, which strongly suggested that two stages of oxygen diffusion may be involved. The full width at half maximum (FWHM) of the $00\underline{38}$ main reflection, which reflects structural distortion in the *c* direction, showed a peak around the optimized oxygen doping. This implies that the structural modification may be another factor that affects T_c apart from oxygen content. On the other hand, the period of incommensurate modulation along the *b* direction, *s*, was found to have nothing to do with the oxygen content or superconductivity. Relationships between superconductivity, oxygen content and microstructure of the Bi2212 single crystal are discussed.

1. Introduction

It is well appreciated that the carrier doping condition plays a crucial role in the normal and superconducting state properties of high-T_c oxide superconductors. In the 85 K superconductor $Bi_2Sr_2CaCu_2O_y$ (Bi2212), Groen and de Leeuw [1] reported that T_c is determined by the hole concentration in the CuO plane, and there is a bell-shaped curve between T_c and hole concentration with a maximum value at about 0.2 holes/Cu per CuO plane. Since hole concentration can be varied by changing the oxygen content, post-heat treatments under different conditions have been widely adopted to study the effect of oxygen doping on superconductivity in the Bi2212 system. Results on Bi2212 polycrystalline samples [2–9] confirmed that T_c depended strongly on oxygen content and there existed an optimum oxygen concentration corresponding to a maximum T_c in the system [5–7], but the optimum amount was quite different according to different authors [2, 5]. Single-crystal samples have many obvious advantages over polycrystalline samples on probing the intrinsic physical properties of Bi2212 superconductor, so recently more experiments have been performed on single crystals. After annealing Bi2212 crystals in 1 atm oxygen or air, several authors [10–15] reported an increase in T_c with annealing temperature, with a maximum value of 92–95 K. However, for Bi2212 crystals annealed under varying oxygen pressure at a certain temperature, contradictory results were reported [16–20]. Mitzi *et al* [16] and Yasuda *et al* [17] reported a decrease in T_c with increasing oxygen pressure,

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contrary to the results reported by Forro *et al* [18], Crommie *et al* [19] and Zhang and Lieber [20]. This could be ascribed to the fact that the hole doping conditions of the as-grown crystals and the heating and cooling rates employed by different authors were different.

On the other hand, the superconductivity of Bi2212 is known to be sensitive to microstructure. To the best of our knowledge, however, full structural characterization of Bi2212 crystals with different oxygen content was absent from most previous works. The exception was that the change in c-axis length with oxygen content has been studied carefully and a certain level of consensus has been achieved [11, 12, 14, 16, 21]. Most results showed that the c-axis length decreases with increasing oxygen content [11, 12, 14, 16]. It is known that the real structure of Bi2212 is very complex due to the existence of the incommensurate modulation [22–25]. The origin of the modulation structure remains a subject of controversy since different models have been proposed, involving cation deficiency [26], influence of the Bi^{3+} lone pair [27–29], extra oxygen in BiO layers [30–32] and lattice mismatch [34–39]. Furthermore, the relation between superconductivity and modulation structure is not very clear. Calestani *et al* [40] found that the non-modulated $Bi_{2-x}Pb_xSr_2Y_{1-y}Ca_yCu_2O_z$ phase still showed superconductivity in the Ca-rich region, supplying an example of superconductivity not being related to structural modulation for Bi2212, but no study on relationships between T_c and modulation for $Bi_2Sr_2CaCu_2O_y$ crystals with different oxygen content has been reported.

In this paper, we systematically study the superconductivity and structural characterization of $Bi_2Sr_2CaCu_2O_y$ single crystals annealed at 600 °C and under a large oxygen pressure range from 10^{-7} to 6080 Torr. With increasing oxygen pressure, two processes of oxygen diffusion occur and lead to a change of carrier concentration. It was found that apart from the oxygen content, structural distortion also affects the superconductivity. The relationships between the modulation period, oxygen content and superconductivity are fully discussed.

2. Experimental details

$Bi_2Sr_2CaCu_2O_y$ single crystals were grown from Bi-rich melts by a directional solidification method with the atomic ratio of the grown melts of 2.4 Bi: 2.0 Sr: 1.0 Ca: 2.0 Cu [41]. To ensure homogeneity of the crystals with regard to the composition, structure and oxygen content, bright crystal sheets of rectangular shape with ab-plane dimensions of 3 mm × 2 mm and thickness around 20 μm were chosen as candidates for the annealing experiments. Before annealing experiments all the crystals were characterized by x-ray diffraction, both the $00l$ diffraction and the rocking curve of the $00\underline{10}$ main reflection, so that highly oriented single crystals with *only* the $00l$ diffraction of the Bi2212 phase were selected. The mosaic spread of our crystals, measured by a θ-scan rocking curve of the $00\underline{10}$ reflection, was about 0.2–0.5°. In a typical annealing experiment, the as-grown crystal was maintained at 600 °C under a certain oxygen pressure (10^{-7}–6080 Torr) for 30 min and then slowly cooled to room temperature in the same atmosphere. The rate of heating to 600 °C, nearly the same as that of cooling, was about 200 °C h^{-1}. For oxygen pressure lower than 1 atm, the crystals were annealed under balanced oxygen pressure in a high-vacuum chamber (base vacuum of 10^{-8} Torr). For oxygen pressure higher than 1 atm, the crystals were annealed in a tube, which was firstly extracted to high vacuum (10^{-5} Torr) and then filled with a certain amount of oxygen. It should be pointed out that the range of annealing conditions falls within the thermodynamic phase stability of Bi2212 [42].

Superconducting transitions of the as-grown and annealed crystals were determined by ac susceptibility measurements with a magnetic field (0.2 Oe, 108 Hz) perpendicular to the

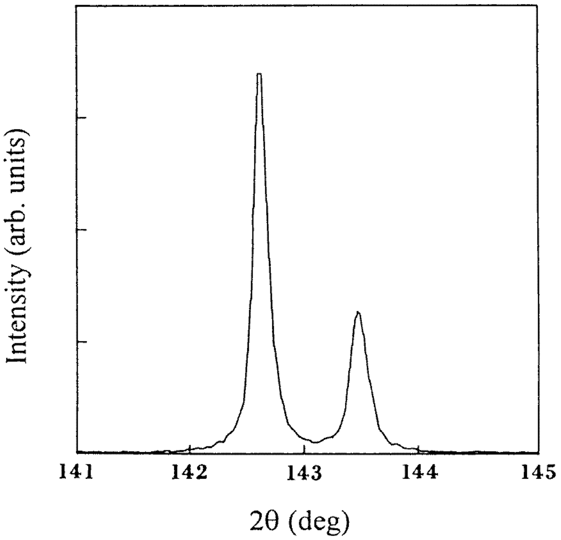

Figure 1. The x-ray $00\underline{38}$ reflection of $Bi_2Sr_2CaCu_2O_y$ single crystals. Double peaks are due to Cu $K\alpha_1$ and Cu $K\alpha_2$ splitting.

crystal basal plane ($H \parallel c$) and a standard lock-in technique was employed. T_c is defined as the onset temperature of diamagnetic transition.

X-ray diffraction data for the crystal before and after annealing were collected using an x-ray rotating-anode diffractometer (D/Max-γA, Rigaku) with graphite monochromatized Cu $K\alpha$ radiation. The cell parameters were determined by main reflections performed on single crystals in reflection or transmission geometry described elsewhere [43]. Since the higher the Bragg angle, the more precise the d value that can be obtained through the Bragg equation, the c-axis parameter was calculated from the $00\underline{38}$ main reflection with a Bragg angle of about 143°, which is near the limit of our diffractometer. The typical $00\underline{38}$ reflection of a $Bi_2Sr_2CaCu_2O_y$ single crystal is shown in figure 1. Double peaks are due to Cu $K\alpha_1$ and Cu $K\alpha_2$ splitting. In this paper, the full width at half maximum (FWHM) of the Cu $K\alpha_1$ peak of the $00\underline{38}$ reflection was studied, for it reflected the lattice distortion in the c-axis direction. The a and b lattice constants were calculated from 400 and 040 main reflections, respectively, measured in transmission. The incommensurate modulation period s can be calculated from satellite reflections. All reflections, taking into account the modulation structure, are indexable with $h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^* + m\boldsymbol{q}^*$ ($\boldsymbol{q}^* = \boldsymbol{b}^*/s$). So the distance from the origin of the reciprocal lattice d^* is given by

$$d^* = 1/d = \left[h^2(1/a)^2 + (k + m/s)^2(1/b)^2 + l^2(1/c)^2\right]^{1/2}$$

where d is the plane interval and is related to the diffraction angle by the Bragg equation. From the observed d value of the 0211 satellite reflection, the modulation period s was calculated.

3. Results and discussion

Figure 2 shows the superconducting transition temperature T_c of Bi2212 single crystals as a function of annealing oxygen pressure P. T_c rises with increasing oxygen pressure and shows a maximum of 91.4 K at $P = 200$ Torr. Then a further increase of oxygen pressure

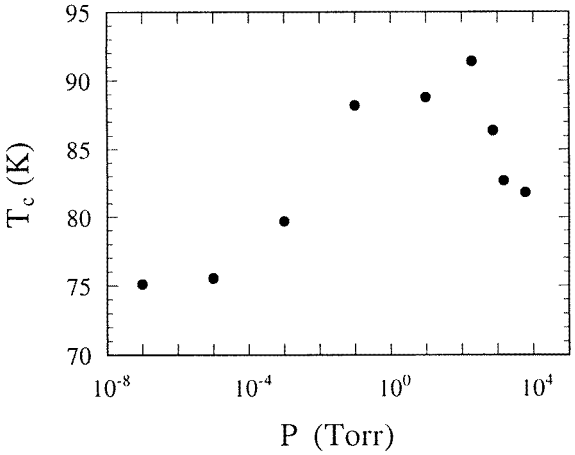

Figure 2. The dependence of T_c on the oxygen pressure P of annealing at 600 °C for $Bi_2Sr_2CaCu_2O_y$ single crystals.

results in rather rapid suppression of T_c. Though we have no means to measure the oxygen content of each crystal since the size of the crystals is not sufficient for thermogravimetric analysis or chemical titration, it is obvious that oxygen content in these crystals ranged from underdoping to overdoping, if a one-to-one correspondence between oxygen content and T_c is assumed.

Figure 3 shows variations of the lattice constants of Bi2212 crystals with oxygen pressure. The change in b-axis value is rather small and does not show any obvious change with the oxygen pressure. The a-axis value shows a weak trend of decrease with increasing oxygen pressure. These mean that the oxygen content in a Bi2212 single crystal has a very small influence on the structure of the ab plane. However, it is clear that the c-axis value changed in two stages with annealing oxygen pressure. The c-axis value hardly changes with increasing oxygen pressure from 10^{-7} to 10^{-1} Torr (stage 1) and decreases sharply with increasing oxygen pressure higher than 10^{-1} Torr (stage 2). Since the average values of Sr/Ca ratio in the lattice may not change after each annealing, the oxygen content may play an important role in variations of the c-axis length. The decrease of c-axis value with increasing oxygen content in the Bi2212 system has been reported by many authors [11, 12, 14, 16]. The possible mechanism for the relation between the c-axis length and oxygen content was discussed by Zandbergen *et al* [27]. In their model extra oxygen can be inserted into the BiO layers and results in a change of the orientation of the Bi^{3+} lone pair, which causes a decrease of the distance of two adjacent BiO layers and so a shrinking of the c axis. Based on the change in T_c with oxygen pressure shown in figure 2, the hole concentration in the CuO planes increases on increasing the extra oxygen in the BiO layers, which can be explained by a self-doping mechanism in band calculations [44, 45]. That means the hole carriers originate from the so-called BiO reservoir [1]. The self-doping mechanism was confirmed experimentally by angle-resolved photoemission [46], Raman [47] and x-ray absorption near-edge [48] spectroscopy. Thus, diffusion of oxygen into the BiO layers is suggested to be responsible for the decrease in c-axis value and variation of T_c in the oxygen pressure range from 10^{-1} to 6080 Torr.

The most particular feature here is the stability of c-axis value with oxygen pressure varying from 10^{-7} to 10^{-1} Torr, while the T_c value increases rapidly in this oxygen pressure

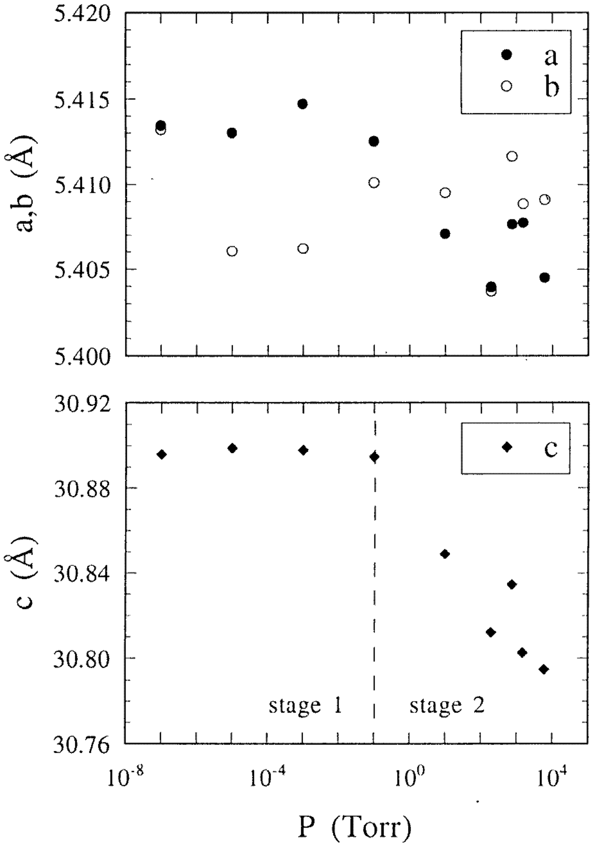

Figure 3. Changes in cell parameters a, b and c with changing annealing oxygen pressure P for $Bi_2Sr_2CaCu_2O_y$ single crystals.

range. No similar result has been reported previously. Because there is always a certain amount of extra oxygen in the BiO layers, it is difficult for outer oxygen to diffuse into the BiO layers when the annealing oxygen pressure is very low. We assume that oxygen diffusion in this stage mainly takes place in CuO planes to occupy the oxygen vacancy in the CuO layers. It is certain that this process hardly changes the cell parameters for the CuO layer is rather rigid, which will be discussed later. The carrier concentration in the CuO layer would increase since one additional oxygen atom creates two holes, which results in the increase of T_c. Li *et al* [21] observed a plateau of c-axis value in $Bi_2Sr_2CuCa_2O_y$ single crystals with increasing ambient temperature. They also explained it as oxygen diffusion in the CuO layer, but in their data, the T_c also showed a plateau, which is difficult to explain. Therefore, with increasing annealing oxygen pressure there may be two stages of oxygen diffusion which affect the carrier concentration and so T_c of the Bi2212 system. However, another factor of influence on T_c should be considered, which deals with the structural modification of Bi2212 single crystals induced by thermal treatment.

Figure 4 shows the change in the FWHM of the $00\underline{38}$ main reflection ($\Delta\theta$) of Bi2212 crystals with annealing oxygen pressure. In the range of oxygen pressure from 10 to 6080 Torr, a peak of $\Delta\theta$ is observed, where the maximum of T_c also occurs. Although the oxygen content in the crystal has great influence on the c-axis length, this kind of lattice

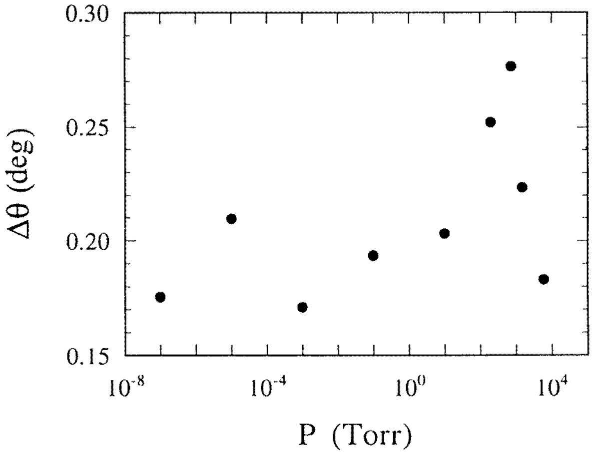

Figure 4. The change in the FWHM of the 00$\underline{38}$ main reflection ($\Delta\theta$) of $Bi_2Sr_2CaCu_2O_y$ single crystals with annealing oxygen pressure P.

distortion in the c direction may be not related to inhomogeneous distribution of extra oxygen in the BiO layers. Previous experiments [13, 15] have shown that the change of superconductivity in $Bi_2Sr_2CaCu_2O_y$ single crystals depended on annealing temperature or pressure rather than on annealing time. For example, for Bi2212 single crystals annealed in air at 500 or 700 °C only for a few minutes, the T_c and ΔT_c values changed rapidly to values of those annealed for several hours [15]. This means that the oxygen diffusion in the annealing process is very fast if the variation of superconductivity is solely determined by oxygen content. In fact, the ΔT_c values of crystals in the present experiment, taken as the temperature difference between 10 and 90% of the full ac susceptible transition, have a small width of no more than 2 K after annealing. So structural distortion in the c-axis direction may be due to the modification of the crystal structure itself in the annealing process, for example disorder of the cation arrangement, rather than due to the possible oxygen inhomogeneity induced by the short annealing time (30 min). As reported by our group previously [13, 49, 50], the surface phase decomposition in the annealing process may relate to variations of superconducting transition of $Bi_2Sr_2CaCu_2O_y$ single crystals. In fact, phase decomposition surely reflects in an indirect way some intrinsic structural modification of Bi2212 phase in the annealing process. Due to the short annealing time (30 min), little segregated phase has been observed in annealed crystals by x-ray diffraction. So the present result shows *directly* that the structure of the $Bi_2Sr_2CaCu_2O_y$ phase is surely modified in the annealing process and is closely related to the change of superconductivity. At present no explanation for the fact that the maximum T_c nearly corresponded to the maximum $\Delta\theta$ is available and further studies are still needed.

Figure 5 shows the modulation period s of Bi2212 crystals annealed under different oxygen pressures. Although oxygen content changes evidently, s changes very little and does not show any dependence on oxygen content. Several models have been proposed for the origin of the structural modulation in the Bi2212 system [26–39]. Yamamoto *et al* [32] pointed out that the existence of excess oxygen in the BiO layers was the major cause for such modulation on the basis of their Rietveld analysis of neutron and x-ray powder diffraction data. In their model, the period of modulation decreases when the excess oxygen increases; however, it is inconsistent with our present result. A more likely

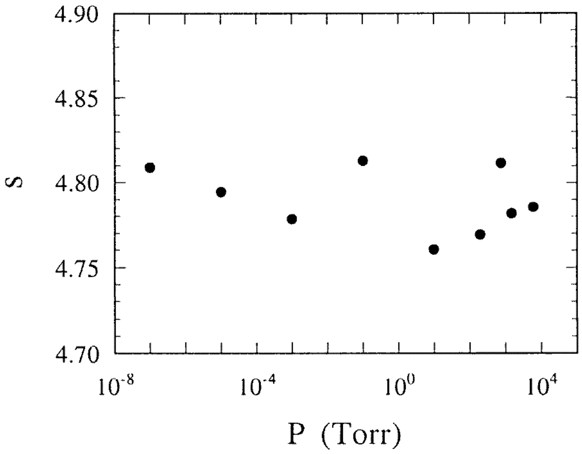

Figure 5. The relation between the modulation period s and the annealing oxygen pressure P for $Bi_2Sr_2CaCu_2O_y$ single crystals.

origin of structural modulation is considered to be the lattice mismatch between the BiO block and the perovskite slab (Sr–Cu–Ca–Cu–Sr) with the latter as the stiffer one [34–39]. The a and b dimensions of the bulk unit cell may be set by the length of the Cu–O bond in the plane and are insensitive to the excess oxygen in BiO layers. Because the Bi ions share common O ions with the CuO plane below and the Cu–O bond is much more rigid, the BiO plane will distort to match the crystal structure imposed by the CuO plane. While the Bi–O bond is rather short, it may expand and buckle to accommodate the CuO plane or the perovskite-related slabs. The extra oxygen then is easy to insert into the distorted BiO layers, and it is a result rather than an origin of modulation structure. On the other hand, the present results also indicate that superconductivity of $Bi_2Sr_2CaCu_2O_y$ has nothing to do with modulation structure.

In a recent report, Yokoya *et al* [51] have pointed out that the superstructure of the BiO layers has no intrinsic correlation with the superconducting gap of $Bi_2Sr_2CaCu_2O_y$ single crystals by an angle-resolved photoemission spectroscopy experiment. So it is reasonable that the modulation structure has little contribution to the superconductivity of Bi2212.

4. Conclusions

High-quality $Bi_2Sr_2CaCu_2O_y$ single crystals annealed at 600 °C under an oxygen pressure range from 10^{-7} to 6080 Torr have been studied carefully by x-ray diffraction and ac susceptibility measurements. The T_c went through a maximum with increasing oxygen pressure. The c-axis value showed a plateau in a large oxygen pressure range, 10^{-7}–10^{-1} Torr, and decreased with increasing oxygen pressure above 10^{-1} Torr, which means that two mechanisms of oxygen diffusion may be involved. The FWHM of the $00\underline{38}$ main reflection showed a peak around the maximum T_c, which reflects that structural modification may be another factor that affected T_c apart from the oxygen content. The modulation period s was found to be loosely related to both oxygen content and superconductivity.

Acknowledgments

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