Annealing temperature and O_2 partial pressure dependence of T_c in $HgBa_2CuO_{4+\delta}$

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Samples of $HgBa_2CuO_{4+\delta}$ (Hg-1201) were annealed under various conditions. After carefully controlling annealing time, annealing temperature (T_a), and O_2 partial pressure (P_0), we were able to find the reversible annealing conditions for Hg-1201. Under 1 atm O_2 at 260 °C$\leqslant T_a \leqslant$400 °C, the obtained T_c is nearly the same (~97 K). However, it decreases quickly with T_a>300 °C in high vacuum ($P_0 \sim 10^{-8}$ atm), and reaches zero at T_a=400 °C. On the other hand, T_c decreases with the decrease of T_a in high-pressure O_2 (~500 atm) and reaches ~20 K at about 240 °C. In the entire annealing region, the oxygen surplus varies significantly from 0.03 to 0.4, and a wide range of T_c variation (0→97 K→20 K) was obtained with anion doping alone.

Hg-1201 has a very simple crystal structure[1] and the highest T_c (~97 K at the optimal doping level) among all the single CuO_2-layer high-temperature superconductors (HTSs). Its simplicity makes it an ideal system for use in verifying theoretical models. For this purpose, doped samples with a wide T_c range to cover both the insulator-superconductor transition on the underdoped side and the superconductor-metal transition on the overdoped side are desirable. Many groups around the world raced to achieve that by annealing the as-synthesized samples in reduced or oxygenated gases. However, only limited results have been reported so far, partially due to Hg loss in this compound at elevated temperatures. Wagner *et al.*[2] reached $T_c \sim 50$ K through reducing annealing in Ar at 500 °C. Itoh *et al.*[3] report at high-pressure O_2 annealing only produced a moderate change of T_c (~85 K on the overdoped side). The search for a wider T_c range has been obstructed by the decomposition of the compound above 500 °C. By studying the stability and the oxygen balance conditions, we explored a much wider annealing temperature-oxygen pressure region. The reversible annealing conditions were established. We obtained underdoped samples with T_c as low as zero (insulator) and heavily overdoped samples with $T_c \sim 20$ K. In other words, the obtained samples cover nearly the whole insulator-superconductor-normal metal phase region. This enables us to further study the superconductivity of this compound in detail.

Hg-1201 samples were prepared by reacting a precursor pellet of Ba_2CuO_x and a composite Hg source. The precursor pellet is obtained by mixing appropriate amounts of BaO and CuO in an alumina crucible in a flowing mixed gas of Ar:O at a ratio of 4:1 at 930 °C for a total of 24 h with intermittent grinding once every 8 h. The composite Hg source used in this study was a prereacted Hg 1:2:0:1 pellet made by compacting the thoroughly mixed HgO and pulverized precursor powder. A small precursor pellet and a large composite Hg source are sealed inside an evacuated quartz tube, heated to about 810 °C and kept at this temperature for 8 h before being cooled to room temperature. Samples with different oxygen content were obtained by heating the as-synthesized samples at different temperatures and oxygen partial pressures for appropriate periods of time. Underdoped samples were prepared by heating the sample in vacuum at temperatures between 250 and 500 °C for 20–80 h. Overdoped samples were obtained by heating the as-synthesized compound for 10–240 h at temperatures between 240 and 400 °C and at an oxygen pressure that was between 1 and 500 bar. The structure was characterized by x-ray powder diffraction (XRD) and neutron powder diffraction (NPD). T_c were determined by both the dc magnetic susceptibility method using a Quantum Design superconducting quantum interference device (SQUID) magnetometer and the electrical resistivity method using the standard four-probe technique.

We knew beforehand that there are two things which may effect the T_c of Hg-1201, oxygen content and mercury loss. We tried to find annealing conditions which allowed any changes in sample structure and T_c to remain reversible. We found that long annealing times and high temperatures lead to mercury loss and sample decomposition. Figure 1(a)

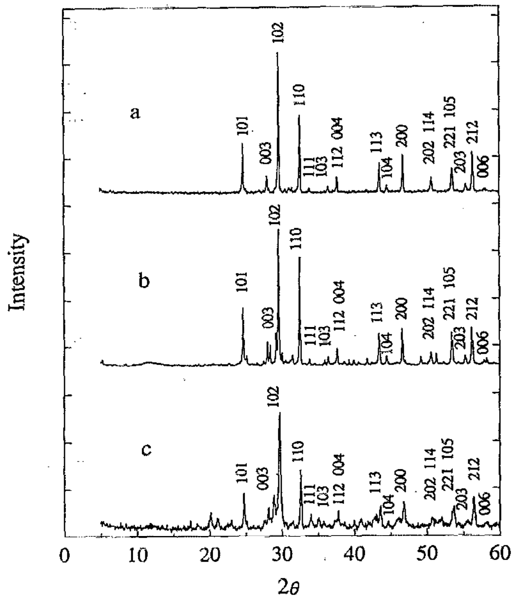

FIG. 1. (a) The indexed x-ray powder diffraction pattern of a typical as-synthesized Hg-1201 sample. (b) The XPD pattern of a Hg-1201 sample after 20 h of 500 °C Ar annealing. (c) The XPD pattern of a Hg-1201 sample after four days of 500 °C Ar annealing.

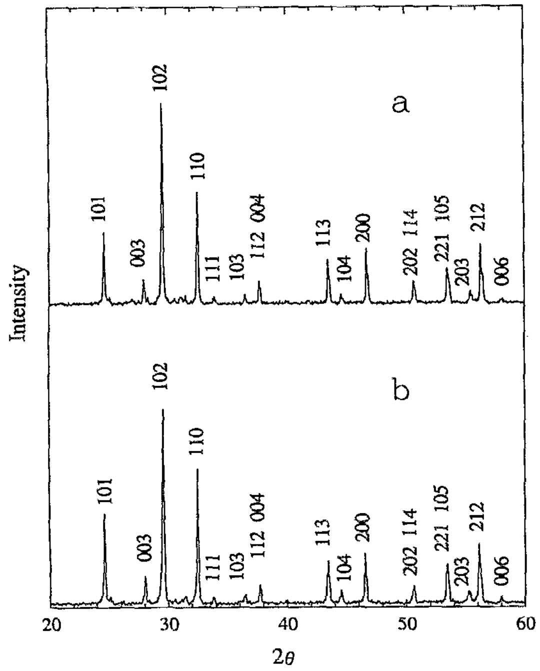

FIG. 2. (a) The XPD pattern of a Hg-1201 sample before annealing. (b) The XPD pattern of a Hg-1201 sample after three days of vacuum annealing at 400 °C.

is the data taken from a sample immediately after it was synthesized. It is almost single phase. Figure 1(b) is data taken from a sample after annealing in Ar at 500 °C for 20 h. A small amount of impurities show up. Figure 1(c) is data taken from a sample after annealing in Ar at 500 °C for about four days. Many impurities now appear. After carefully controlling annealing time and temperature, we were able to find the reversible annealing conditions for Hg-1201. Some typical x-ray data are shown in Fig. 2. Figure 2(a) was taken before annealing and Fig. 2(b) was taken after three days of annealing in vacuum at 400 °C. These data indicate that the sample still had a single Hg-1201 phase after the anneal. The slight shift in the peaks was caused by the change in lattice parameters that arose from the change in oxygen content of the sample. It is clear that the change in structure is reversible under these conditions.

Figure 3 shows resistivity data for one of our samples. Line 1 is data taken from the sample immediately after it was synthesized. Line 2 is data taken after a 240 °C, high-pressure (P=500 bar) anneal. After this, we annealed the sample again in one atmosphere of oxygen at 300 °C. Resistivity data taken after this second annealing are plotted here as line 3. These data show that the change in T_c was reversible and the T_c drop was caused by oxygen doping alone. The small transition broadening and change in resistivity were probably due to mercury loss between boundaries. The Meissner effect of this sample, which is shown in the inset of Fig. 3, is also consistent with this point.

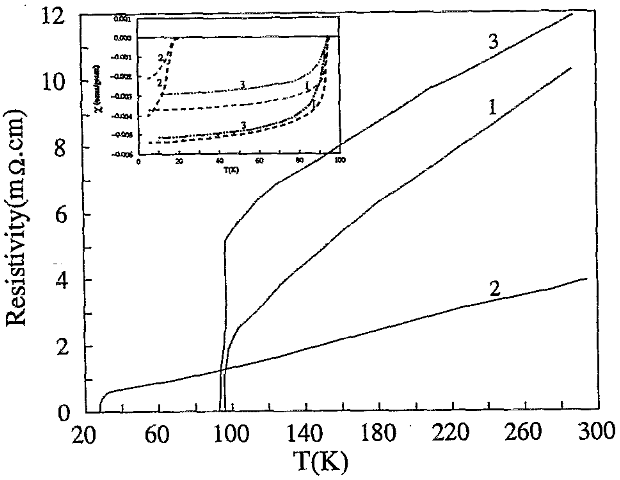

FIG. 3. Typical resistivity data taken from our Hg-1201 samples. Line 1 was taken immediately after the sample was synthesized. Line 2 shows data taken after a 240 °C, high-pressure (P=500 bar) anneal. Line 3 was taken after an anneal in 1 atm of oxygen at 300 °C.

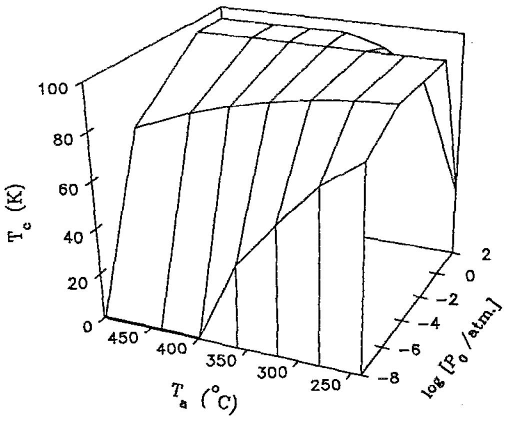

FIG. 4. 3-D T_c vs (T_a, log P_0) for Hg-1201.

The reversible annealing conditions are summarized in Fig. 4. The annealing time t, which should be long enough to let oxygen reach an equilibrium state but avoid significant Hg loss, is about 10–240 h, depending on the annealing environment. The T_c corresponding to the desired T_a- log P_0 conditions are obtained by interpolation. From the thermodynamic viewpoint an increase in annealing temperature should result in a decrease in oxygen content if the oxygen partial pressure is held constant. An increase in oxygen content should result from an increase in oxygen partial pressure if the annealing temperature is kept constant. When the sample is annealed in vacuum (10^{-8} atm) T_c decreases when the oxygen content decreases. This indicates that the sample is in its underdoped region. T_c increases with increasing annealing temperature when the sample is annealed in high-pressure oxygen ($5\times10^{+2}$ atm). This means that the sample is in the overdoped region. T_c is nearly the same over the range 250–400 °C in 1 atm of pure O_2. We were able to obtain T_c's ranging from 0 in the underdoped region to 97 K (optimal), then back down to 20 K in the overdoped region. According to an earlier study,[4] when the oxygen partial pressure is changed from 1 to 10^{-5} atm the oxygen content changes by about 0.4 for Y123. This means that the oxygen content is sensitive to the oxygen partial pressure in

$YBa_2Cu_3O_{7-\delta}$ (Y123). Comparing the annealing conditions with our thermogravimetric analysis and NPD results,[5] we found that when P_0 changes from $5\times10^{+2}$ to 10^{-8} atm, δ changes by about 0.4. This shows that the δ range is $0<\delta<0.4$, which is similar to that in Y123 but depends only weakly on P_0, which contrasts with Y123. The carrier concentration p has been determined, based on the room-temperature thermoelectric power and roughly follows $p\sim0.72\delta$; details will be published elsewhere.[5]

In summary, we have explored the reversible annealing conditions for Hg-1201 and obtained a T_c that covers the widest variation ever by anion doping only. Though the δ range in Hg-1201 is similar to that in Y123 we found that the sensitivity of δ to changes in oxygen partial pressure is much smaller than in Y123.

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