RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 7 1 SEPTEMBER 1988

Thermal recovery of oxygen-deficient superconducting $YBa_2Cu_3O_{7-\delta}$ oxides in ambient oxygen

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(Received 21 March 1988)

We have annealed the oxygen-deficient ceramic oxide $YBa_2Cu_3O_{7-\delta}$, where $\delta = 0.4$, in ambient oxygen to obtain in-diffusion of oxygen. *In situ* resistivity measurements were used to monitor annealing at constant heating rates between room temperature and 570 °C. The resistivity curve showed a maximum and a minimum. The temperatures where the maximum and the minimum were observed change with heating rate. By measuring their dependence on heating rate, which was varied from 15 to 0.1 °C/min, we have determined the activation energy of oxygen diffusion in the oxide ($\delta = 0$) to be 1.35 ± 0.10 eV. The in-diffusion is limited by a near-surface layer which requires the measured activation energy for oxygen to diffuse through it.

A two-step thermal process has generally been found to be essential in fabricating the superconducting $YBa_2Cu_3O_{7-\delta}$ oxides, whether they are in bulk or in thin-film form.[1,2] The first step is a high-temperature sintering treatment near 950 °C in oxygen (or air) and the second step is a low-temperature anneal near 500 °C or alternatively a very slow rate of cooling in ambient oxygen. Why this two-step heat treatment is essential to the superconducting oxide formation is not well understood; perhaps it could be explained on the basis of cation and anion diffusion. Typically, anions move much faster than cations in a perovskite-type oxide, especially if it is defective and oxgyen deficient.[3] The high-temperature sintering orders the cations, i.e., synthesizes the crystal structure and allows grain growth. The low-temperature anneal is to replenish oxygen into the high-temperature structure, which is highly oxygen deficient. Since oxygen stoichiometry affects T_c,[4-6] we must readjust the oxygen content properly by the in-diffusion of oxygen.

While there are now a variety of ways of preparing the oxide, e.g., mixing and firing powders, codeposition or sputtering films on single-crystal substrates, reaction of layered thin films, and wet chemical methods, the low-temperature step of optimizing the superconducting properties of the oxide is still mostly performed by trial and error. This is because of the lack of detailed knowledge of oxygen diffusion and solution in the oxide. The optimal condition may vary from sample to sample according to the effects of grain size, preferred orientation of grains, density and interconnecting voids, and the presence of any surface and grain boundary phase, yet the controlling kinetic parameters are oxygen diffusivity and solubility in the oxide. In this Rapid Communication, we illustrate the in-diffusion behavior of oxygen in oxygen-deficient bulk and polycrystalline $YBa_2Cu_3O_{7-\delta}$ samples by using *in situ* resistivity measurements. Since the resistivity of these oxides is affected by the oxygen deficiency δ,[7] we can probe the change in δ by analyzing the change in resistivity during the oxygen diffusion process and determine the activation energy of oxygen diffusion in the oxide.

Experimentally, we began by thermally driving oxygen out of the oxide samples which have $\delta = 0$, $T_c = 91$°K, grain size about 5–10 μm, and a large amount of interconnecting voids. This was carried out by annealing the samples in helium at a constant heating rate of 3 °C/min ramping from room temperature to 500 °C and followed by furnace cooling to room temperature. This degradation condition produced $\delta = 0.4$ in the oxide measured by weight lost and was reproducible, especially when a single sample was used repeatedly. Annealing in He to higher temperatures was avoided since the oxygen departure rate becomes extremely fast and the loss of a huge amount of oxygen might induce undesirable phase changes in the oxide. Our purpose for degrading the oxide is just to remove some oxygen without structural change. After the degradation, we recovered the lost oxygen by annealing the samples in ambient oxygen of atmospheric pressure from room temperature to 570 °C at various heating rates. *In situ* resistivity and weight-gain measurements were used to monitor the time and temperature needed for the recovery. The superconducting state was checked by T_c determination. Details of the sample preparation and resistivity measurement have been reported previously.[7]

In Fig. 1, the solid curve shows thermal degradation in helium of an oxide sample beginning with $\delta = 0$. The arrows and numbers show the directions of temperature changes and sequences of annealings, respectively. The sequence went from 1 to 2 in helium, then from 3 to 4 in oxygen. The solid curve, which started at the lower-left corner and advanced with a ramping rate of 3 °C/min, shows a linear increase of resistivity with temperatures up to 350 °C and a nonlinear increase thereafter. This behavior is typical of annealing $YBa_2Cu_3O_{7-\delta}$ in He. At 500 °C, the cooling began and the curve turned around but the resistivity still went up due to a continuing out-diffusion of oxygen. Then, the curve went downward until 350 °C where out-diffusion of oxygen stopped. After that the decrease of resistivity became linear with temperature, however, with a slope that is much greater than the initial one of heating in the same temperature range. The change in slope suggests that the temperature coefficient

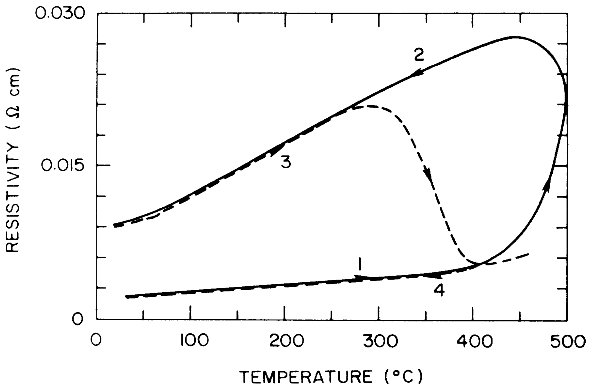

FIG. 1. The solid curve shows the resistivity change of an oxide sample with $\delta = 0$ during a ramp annealing in helium from room temperature to 500 °C and cooling back to room temperature. The ramping rate was 3 °C/min. The arrows on the curve show the directions of temperature changes. The dashed curve shows the behavior of the oxygen-deficient sample during annealing in oxygen ambient from room temperature to 450 °C at a rate of 1 °C/min and cooling back to room temperature.

of resistance for the sample of $\delta > 0$ is larger than that of $\delta = 0$, which is intriguing. Yet, the curve bent upward around 80 °C and followed a smaller slope to room temperature. After the cyclic annealing, we measured a weight loss of 1%, corresponding to $\delta = 0.4$.

The recovery in ambient oxygen with a heating rate of 1 °C/min, shown by the dashed curve in Fig. 1, began at the place where the annealing in helium ended. It more or less retraced the solid resistivity curve in going up, but the bend at 80 °C is more pronounced. It turned downward around 300 °C and then decreased to a minimum around 410 °C. Beyond the minimum, the resistivity increased. In cooling, it followed the lower dashed line to return to the very beginning. After the recovery was completed, δ was found to return to zero by weight-gain measurement and T_c was determined to have the initial value of 91 K.

We shall now concentrate on the recovery process. The upper dashed curve shows first a bend, then a maximum, and finally a minimum in resistivity. About the bend, we postulate that it is due to order-to-disorder transition of oxygen vacancies in the CuO plane. Details of the energetics, ordered structure, and kinetics of the transition will be reported separately. After the bend, the linear increase of resistivity with increasing temperature can be attributed to the metallic behavior of the oxide. As the temperature became high enough for a sufficient amount of in-diffusion of oxygen to take place, the dashed curve started to peel downward from the solid curve because of the increase of carrier concentration in the oxide. At the maximum, the metallic behavior is offset by the increase of carriers. Beyond the maximum, the resistivity came down with δ as more in-diffusion of oxygen had occurred. It reached the minimum, beyond which the resistivity went up again with temperature. The resistivity would also go up if the oxide loses oxygen to its ambient, but it has been shown that the oxide is quite stable in ambient oxygen up to 500 °C.[8] We note that the minimum is well defined and can be determined rather precisely.

The temperature at which the minimum resistivity occurs is a function of heating rate; the faster the heating rate, the higher the temperature, as shown in Fig. 2 where a plot of three recovery runs of 10, 1, and 0.1 °C/min is shown. Since a faster heating rate means a shorter time of annealing, a faster rate requires a higher temperature than that of a slower rate for oxygen diffusion to saturate the oxide. The temperature of the minimum therefore manifests the completion of in-diffusion oxygen in the oxide as δ approaches zero. Consequently, we can measure the dependence of the minimum on heating rate to determine the activation energy of oxygen diffusion.

To consider the kinetics of in-diffusion, we note that the oxygen diffusion in the oxide is highly anisotropic and occurs mainly in the CuO plane which is between two BaO planes. We define J as the atomic flux, i.e., the number of diffusing oxygen atoms per cm^{2}sec; N_v as the number of oxygen atoms in the CuO plane per cm^3; and δ as the concentration (or fraction) of missing oxygen atoms in the CuO plane, in other words it is just a number varying from 0 to 1. Now if we assume that the in-diffusion is a non-steady-state process, the total number of oxygen atoms diffused into the oxide per unit area over the entire period t of in-diffusion is given by the equation

$$\delta N_v = \int_0^t -(\nabla\cdot J)\,dt\,, \qquad (1)$$

where $J = -D\partial(\delta N_v)/\partial x$ is the atomic flux, $D = D_0 \times \exp(-E/k_BT)$ is the oxygen diffusivity in the oxide, and E is the activation energy of diffusion. At constant heating rate, i.e., $dT/dt = \text{const}$, the solution of Eq. (1) can be obtained by following Ozawa's thermal analysis[9,10] to be

$$\delta\left(\frac{dT}{dt}\right) = \left(D_0\frac{\partial^2\delta}{\partial x^2}\right)\left(\frac{k_BT_{\min}^2}{E}\right)\exp(-E/k_BT_{\min})\,, \qquad (2)$$

where $T_{\min}$ is the temperature of minimum resistivity. In obtaining Eq. (2), the two assumptions made are E is a constant and $\partial^2\delta/\partial x^2$ is a slowly varying function of tem-

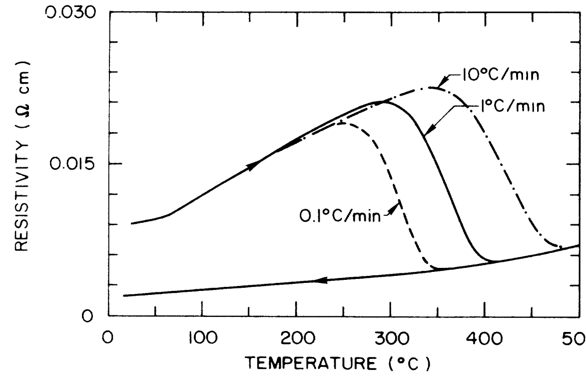

FIG. 2. A set of thermal recovery curves of oxygen-deficient samples ($\delta = 0.4$) upon annealing in ambient oxgyen at 10, 1, and 0.1 °C/min heating rates. The temperature of the minimum resistivity increases with increasing heating rate.

perature. These assumptions will be justified later. Also, the solution is given in the one-dimensional form assuming that the grains in the sample are randomly oriented. On the basis of Eq. (2), E can be measured by plotting $\ln[(dT/dt)/T_{\min}^2]$ vs $1/k_B T_{\min}$, or by plotting $\ln(dT/dt)$ vs $1/k_B T_{\min}$ since $T_{\min}$ does not vary much as compared to dT/dt. A plot of both, the latter in solid circles and the former in open circles, from eight runs of heating rate of 14.7, 10.8, 6.5 3, 1, 0.64, 0.3, and 0.1 °C/min is shown in Fig. 3. The slope of the lines, which are a least-squares fit to the data, delivers activation energies of 1.35 and 1.23 eV, respectively, from the plot of $\ln(dT/dt)$ vs $1/k_B T_{\min}$ and the plot of $\ln[(dT/dt)/T_{\min}^2]$ vs $1/k_B T_{\min}$.[11–13] The uncertainty of these measurement is ± 0.1 eV, and the measured activation energy is insensitive to the initial value of δ as indicated by Eq. (2).

For comparison, we also show in Fig. 3 the plot of $\ln[(dT/dt)/T_{\max}^2]$ vs $1/k_B T_{\max}$ and the plot of $\ln(dT/dt)$ vs $1/k_B T_{\max}$ of the same eight runs, where $T_{\max}$ is the temperature of maximum resistivity, and the slopes yield activation energies of 1.33 and 1.25 eV, respectively, which are practically identical to those obtained from $T_{\min}$. It indicates that even in the early stage of in-diffusion, a near-surface layer saturated with oxygen ($\delta = 0$) has been developed and this layer limited the in-diffusion of oxygen with an activation energy of 1.33 eV (or 1.25 eV), so the assumption that E is constant throughout the process is justified. Although the layer thickens with temperature (or time), the oxygen concentration gradient in the layer does not vary much, so the other assumption that $\partial^2\delta/\partial x^2$ is a slowly varying function of temperature can also be justified. The formation of this near-surface layer is due to the in-diffusion of oxygen from room temperature to $T_{\max}$. It has been reported that during the very initial stage of diffusion of oxygen into an oxide of $\delta = 0.38$ at constant temperatures from 210 to 360 °C, the rate is extremely fast and the activation energy of the process is only 0.5 eV.[14] Taking this value, we can estimate that the low-temperature diffusion of oxygen is more than enough to form the near-surface layer.

To determine if the value of 1.35 eV (or 1.23 eV) is physically reasonable, we demand that, for example, in the case of 1 °C/min annealing, oxygen atoms must be able to diffuse across the radius of grains in a few minutes at the minimum temperature. If we use the simple relation of $x^2 = Dt$ and take $x = 5\times 10^{-4}$ cm and $t = 100$ sec, a value of $D = 2.5\times 10^{-9}$ cm²/sec is obtained. Now we evaluate $D = D_0 \exp(-E/k_B T)$, where $E = 1.35$ eV (1.23 eV) and $T = 410$ °C and we obtained $D = D_0 \times 10^{-9.8}$ cm²/sec ($= D_0 \times 10^{-9}$ cm²/sec). These two values of D are comparable, provided that the pre-exponential factor is not unusually large or small for oxygen diffusion. For the other heating rates, a similar agreement can also be shown.

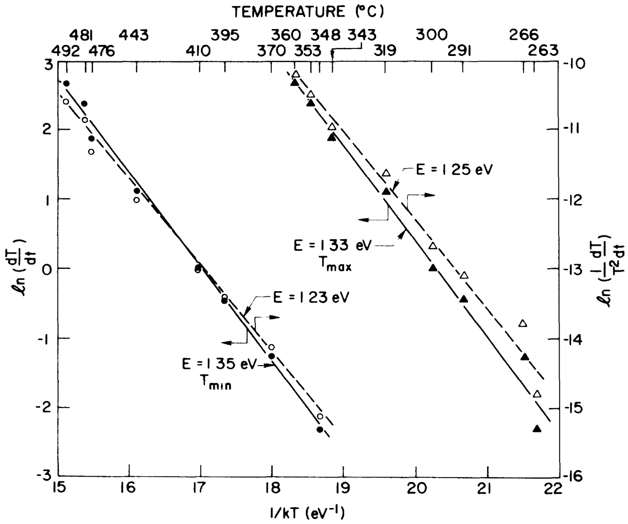

FIG. 3. The plots of $\ln(dT/dt)$ vs $1/k_B T_{\min}$ (the solid circles), $\ln[(dT/dt)/T_{\min}^2]$ vs $1/k_B T_{\min}$ (the open circles), $\ln(dT/dt)$ vs $1/k_B T_{\max}$ (the solid triangles), and $\ln[(dT/dt)/T_{\max}^2]$ vs $1/k_B T_{\max}$ (the open triangles), where $T_{\min}$ and $T_{\max}$ are the temperatures of the minimum and the maximum resistivity, respectively, measured at the eight different heating rates given in the text are shown. The activation energies obtained from the slope of the lines are indicated.

In summary, we have demonstrated the in-diffusion behavior of oxygen in oxygen-deficient samples by using *in situ* resistivity measurement. The resistivity shows a maximum and a minimum. From the temperature dependence of the maximum and the minimum on heating rate, we have determined the activation energy of oxgyen diffusion in the oxide to be 1.35 ± 0.10 eV by applying Ozawa's thermal analysis. We have also found that to replenish oxgyen into the oxide starting from room temperature, a near-surface layer which is saturated with oxygen ($\delta = 0$) exists and acts as a diffusion barrier with the measured activation energy to limit the diffusion of oxygen into the interior of grains.

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