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Anisotropic oxygen diffusion in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ single crystals

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Abstract

The weight change of Bi-2212 single-crystalline samples as a function of temperature, time and surrounding atmosphere was investigated by a classical thermogravimetric technique. Clear evidence for a correlation between T_c and the c -axis lattice parameter was obtained. A plateau was observed in the dependence of T_c and the c -axis lattice parameter on the oxygen contents. From the size dependence it was concluded that oxygen out-diffusion takes place in the a - b plane in a quite anisotropic way, i.e. mainly along the a -direction. At 500°C $D_a/D_b \geq 5$ –6, $D_{ab} \approx 6.12 \times 10^{-8} \text{ cm}^2/\text{s}$.

1. Introduction

It is well known that the oxygen content plays a central role in the normal and superconducting properties of the high- T_c superconducting oxides. Much effort has been spent to study oxygen diffusion in these oxides by thermogravimetric analysis [1,2], in situ resistance measurements [3–6], electrochemical methods [7], and thermal dilatation measurement [8]. Trace diffusion of oxygen in YBCO and Bi-2212 single crystals has also been reported [9–11]. However, for Bi-2212 phase it is noticed that the oxygen-diffusion data, including the amount of oxygen change given by different authors [12–18] do not agree with each other. On the other hand, a similar difference

for oxygen out- and in-diffusion has been observed by in-situ resistance measurement in YBCO [5] and Bi-2212 [6], respectively, but there remains some confusion about the interpretation of the in- and out-diffusion mechanism.

Compared with other methods, a classical thermogravimetric technique can be more accurate and direct in determining the amount of oxygen change and in studying the anisotropy of oxygen diffusion. But when polycrystalline samples are used, the evaluation of absorbed gases will become a problem, especially regarding CO_2 and H_2O . This is because the oxygen change in the Bi-2212 phase is much less compared to the YBCO compound, and, in addition, a polycrystalline sample has a large surface and a great amount of pores. The total amount of these gases would be at least several times larger in weight than

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that of oxygen. Secondly, we cannot exclude a contribution of grain-boundary diffusion in polycrystalline samples. It is also not possible to clarify the structural anisotropy of the oxygen diffusion. For the calculation of the diffusion coefficients, the determination of the effective diffusion lengths is still a question to be solved. Therefore the use of single-crystalline samples is extremely desirable. In this paper, we report on the first very accurate investigations of the weight change of Bi-2212 single-crystalline samples as a function of temperature, time and surrounding atmosphere by thermogravimetric techniques.

2. Experimental

Bi-2212 single-crystalline samples were prepared by the travelling solvent floating zone (TSFZ) method [19]. The compositions were determined from electron probe micro analysis (EPMA) to be $\text{Bi}_{2.17}\text{Sr}_{2.03}\text{Ca}_{1.00}\text{Cu}_{2.00}\text{O}_{8+x}$. The single crystallinity of the samples was checked by X-ray Laue measurements. From both the X-ray and EPMA analyses, it followed that the single-crystalline samples used in the present study are pure Bi-2212 single phase; no evidence of impurity phases was observed.

In order to investigate the mechanism and structural anisotropy of the oxygen diffusion, two samples were prepared: sample A consisting of a number of crystals of typical size $1 \times 1 \times 0.01 \text{ mm}^3$, total weight 178.00 mg, and sample B consisting of a number of crystals of typical size $3.5 \times 1.2 \times 0.1 \text{ mm}^3$, total weight 203.80 mg. The dependence between crystal size and timescale for oxygen out-diffusion in nitrogen atmosphere at 500°C was studied. Although large single crystals of Bi-2212 with a size up to $16 \times 5 \times 1.5 \text{ mm}^3$ have been grown using the TSFZ method [19], for the present measurements, the single-crystal sizes have been chosen as above in order to minimize the problem arising from microcracks in the crystals. The larger the thickness of the grown single crystals, the more serious the microcrack problem. The microcracks are mainly caused by (1) a very weak binding force between the two Bi–O layers; (2) the large thermal stress due to the high radial and axial temperature gradients during the crystal growth; (3) the mechanical stress produced by sawing a rod and cleaving crystals from the sections of the rod.

Thermogravimetric analysis (TGA) was performed using a thermogravimetric microbalance (Setaram TGA 24 thermoanalyzer) connected with a gas mixture system. This thermobalance is able to detect a weight change within $\pm 2.5 \mu\text{g}$. For samples of the Bi-2212 phase of about 200 mg, it is possible to measure the change of Δx with an accuracy of about 0.001. Although the stability range of the Bi-2212 phase is much wider, the experimental temperature range was restricted to between 500 and 800°C . This was done in order to avoid accidental decomposition of the sample at higher temperatures and to minimize the uncertainties arising from other gases absorbed at lower temperatures on the sample surface and the sample holder.

The as-prepared single crystals, sample A and sample B, were first accurately weighed and placed in two small aluminium-oxide crucibles in air before the temperature was raised to 500°C . After equilibrium in air at this temperature was obtained, two different sets of experiments were performed for sample A. In the first set the sample was heated in air to 600 , 700 , 800°C and then cooled to 700 , 600 , 500°C . The succeeding weight changes at each temperature were recorded as a function of time until the sample reached a new equilibrium weight. In the second set of experiments, air was first replaced by 1 bar nitrogen at 500°C . After equilibrium was reached, the sample was heated in 100°C steps to 600 , 700 , and 800°C and again the subsequent weight changes were recorded as a function of time. The partial pressure due to oxygen expelled from the sample is negligible.

For sample B, isothermal oxygen out- and in-diffusion measurements were carried out by introducing nitrogen and reintroducing oxygen at a temperature of 500°C and recording the resulting weight changes versus time. After each set of measurements, the empty crucible was run again in the same procedures as mentioned above. The data presented below were determined by subtracting these empty runs from the runs with samples.

A reference point is needed in order to determine the absolute values of the oxygen contents. Different techniques such as hydrogen reduction, carbon reduction and iodometric titration have been developed. The problem is that two independent techniques even applied on a single batch of samples, still gives quite different results. This difference may arise

from uncertainties inherent to the analytical methods. However, the real reasons are still not known. Therefore we chose the oxygen content at 500°C in air as a reference point.

Using one piece of single crystal (size $3 \times 1 \times 0.1$ mm³), both the superconducting transition temperature T_c and the lattice parameters at each oxygen content were determined by AC susceptibility measurements and X-ray diffraction analyses. The AC susceptibility was measured in an AC magnetic field of 1 G and a frequency of 90 Hz, the X-ray diffraction analyses were performed on a Philips PW-1710 diffractometer using Cu K α radiation and silicon as an internal standard.

3. Results and discussion

The weight change of sample A subjected to temperature cycling between 500 and 800°C in air is shown in Fig. 1. It is noted that no irreversible weight change was observed. The corresponding transition temperature and the lattice parameters also were reversible. This confirms that at each temperature we are measuring the equilibrium oxygen concentration. The change in oxygen composition is defined as $\Delta x = x_{500[\text{air}]} - x_{[T]}$. It should be mentioned that the Δx also depends on the cation concentration of the Bi-2212 phase [19]. It means that Δx can be different even at the same annealing temperature for different Bi contents and Sr/Ca ratios (all normalized to Cu=2). It can also be seen, from Fig. 1, that the

Fig. 1. The weight change with respect to the weight at 500°C (+) and temperature (●) of sample A versus time for cycling between 500 and 800°C in air.

oxygen out- and in-diffusion proceeds quite rapidly with almost the same timescales. This suggests that in this temperature range the oxygen out- and in-diffusion in air is controlled by the same mechanism.

The results of AC susceptibility and X-ray diffraction measurements are shown in Figs. 2(a) and (b). It can be seen that small changes in the oxygen content cause significant changes in T_c and the lattice parameter of the c -axis (Δc is defined as $\Delta c = c_{[T]} - c_{[500]}$). High-resolution electron microscopy [20], neutron [21] and X-ray diffraction [22] studies of Bi-2212 have suggested that there exists an excess of oxygen in the Bi-O layers for samples prepared in air or under a high oxygen pressure. Previous studies have also suggested that oxygen doping in Bi-2212 occurs through loss or gain of oxygen in the Bi-O layers and that these variations are respon-

Fig. 2. The relationship of (a) the superconducting transition temperature $T_{c \text{ onset}}$ and (b) the change in c -axis lattice parameter c with the oxygen loss Δx for two different cation concentrations of the Bi-2212 phase: (I) $\text{Bi}_{2.16}\text{Sr}_{1.91}\text{Ca}_{1.03}\text{Cu}_2\text{O}_{8+x}$ (II) $\text{Bi}_{2.17}\text{Sr}_{2.03}\text{Ca}_{1.0}\text{Cu}_2\text{O}_{8+x}$. Note the definitions of Δx and Δc : $\Delta x = x_{[500]} - x_{[T]}$, $\Delta c = c_{[T]} - c_{[500]}$.

sible for the changes in T_c and the c -axis lattice parameter [16]. Anisotropic tracer diffusion results [11] have shown that oxygen diffusion is highly anisotropic, with $D_{ab} \gg D_c$. Therefore, the oxygen diffusion in the a - b plane direction is expected to dominate the c -axis diffusion (the anisotropy of the oxygen diffusion is discussed in more detail below). The presence of an interstitial oxygen atom in the Bi-O layers [20–22] further indicates that the diffusion along the a - b plane (Bi-O layers) takes place by an interstitial mechanism. No formation energy is needed, the activation energy in air only consists of a kinetic contribution. The fact that the oxygen out- and in-diffusion is quite rapid supports this idea.

Fig. 3 depicts the weight change of sample A versus time after this was subjected to a change of surrounding atmosphere from air to nitrogen at 500°C and subsequently to a change of temperature in steps of 100°C from 500 to 800°C. From the equilibrium values at the different temperatures, Δx can be determined. It is noted that: (1) the observed Δx in nitrogen is much larger than that in air, (2) the time scale of oxygen out-diffusion is much longer than that in air, (3) the samples begin to decompose when the annealing temperature is higher than 700°C. Below 700°C in nitrogen, no decomposition products were found by X-ray diffraction analyses.

From Figs. 2(a) and (b), it is seen that with increasing oxygen loss T_c and the c -axis lattice parameter change simultaneously. In stage 1 they both increase until they reach a maximum at $\Delta x = 0.033$,

Fig. 3. The weight change (+) of sample A versus time after this was subjected to a change of surrounding atmosphere from air to nitrogen and subsequently to a change in temperature (●) in nitrogen from 500 to 800°C.

corresponding to the equilibrium composition in air at 800°C. Upon further increase of Δx to 0.094 (stage 2, the plateau regime) achieved by heating in nitrogen up to 600°C, T_c and the c -axis lattice parameter remain constant. Finally in stage 3, above $\Delta x = 0.094$, they both decrease simultaneously. To our knowledge, this is the first time that stage 1 and 2 have been clearly separated.

It follows from comparison of Figs. 1 and 3 that the equilibrium time in stage 2 is much larger than in stage 1 suggesting that two different mechanisms of oxygen loss and oxygen diffusion are involved (see also section 4). As will be discussed below, we think that in stage 1 oxygen is removed from the interstitial site between the Bi-O layers (site A), whereas in stage 2 it comes out of the Cu-O layers (site B).

The one-to-one correspondence between T_c and c (the c -axis lattice parameter) in stages 1 and 2 suggests that the changes T_c are predominantly controlled by the change of c , irrespective of the reason for these changes. These can be a difference in cation concentration or a small variation of the A site oxygen content. Both have proven to give rise to changes of c and corresponding changes of T_c [19,16] which make the T_c of Bi-2212 very structure sensitive. Further support for the above suggestion comes from high pressure studies on Bi-2212 [23,24]. The negative variations of T_c and $\Delta c/c$ with the pressure p_c along the c -axis, namely $dT_c/dp_c = -18$ K/GPa [23] and $d(\ln c)/dp_c = -6.2 \times 10^{-3}$ /GPa [24], can be combined to

$$dT_c/d(\ln c) = 2.9 \times 10^3 \text{ K}. \quad (1)$$

From Eq. (1) and a measured change $\Delta c = 0.15$ Å at $c = 30.76$ Å, we estimate that $\Delta T_c = 12.6$ K. This agrees quite nicely with our experimental result $\Delta T_c = 12$ –13 K shown in Fig. 2.

As it is generally accepted that T_c in the high-temperature superconductors is governed by the hole concentration in the Cu-O layers [25,26], the above scenario requires an explanation why in the case of Bi-2212 the hole concentration merely depends on c . Though we cannot provide a microscopic explanation, there is a lot of evidence that supports this point. In the first place, the hole carriers in Bi-2212 originate from the Bi-O reservoir, i.e. a self-doping mechanism [16]. It should be noted that the self-doping mechanism in Bi-2212 is quite different from the

doping mechanisms in $\text{La}_{2-y}\text{Sr}_y\text{CuO}_{4+x}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ where the holes are created by substitution or oxygen non-stoichiometry. This feature is experimentally confirmed by angle-resolved photo emission [27], Raman [28] and X-ray absorption near-edge [29] spectroscopy. In the second place, electronic band-structure calculations [30–32] show that changes in the c -axis lattice parameter lead to a redistribution of holes between the Bi–O and Cu–O layers. In addition, calculation of the bismuth valency from the rules of Zachariase [33] and the parameters as given by Brown and Altermatt [34], leads to a relatively large increase of about 0.4 in the bismuth valency when a decrease of 0.1 Å in the Bi–O bonds of 2.2 Å along the c -axis is assumed [35]. Putting all pieces together, we conclude that the removal of oxygen from the A site is responsible for the increases in c and T_c in stage 1 of the annealing study depicted in Fig. 2. Apparently, the oxygen in stage 2 comes from another site. We suggested that it comes from site B, in the Cu–O layers, since a similar plateau in c and T_c versus oxygen content has been observed by Gonzalez-Calbet et al. [36] who simultaneously investigated the influence of the oxygen concentration on the bulk pinning force. They found that the ratio of the maximum pinning forces for unreduced and reduced Bi-2212 scales as the square root of the vacancy density ratio in the Cu–O layers. This agrees nicely with the prediction for flux pinning by oxygen vacancies in the Cu–O layers [37], therefore sustaining the case of oxygen loss from site-B in stage 2. It seems that this conclusion is inconsistent with the observations of Wu et al. [38]. They could not detect from their scanning tunneling microscopic (STM) studies on oxygen-deficient, nonsuperconducting Bi-2212 and a superconducting single crystal with $T_c = 85$ K, any differences in the local electronic and atomic structure in the Bi–O layers. We think, however, that the oxygen loss from the A site is too small to be detected by STM, while the technique cannot probe losses from the B site.

4. Oxygen diffusion

We now turn to the study of the anisotropic oxygen diffusion. As can be seen in Fig. 4, the time scale for oxygen out-diffusion in nitrogen at 500°C is size de-

Fig. 4. The size dependence (sample A and sample B) of the timescale for oxygen out-diffusion at 500°C in nitrogen. The arrows indicate the relaxation time t .

pendent. If the oxygen out-diffusion would be in the c -direction, the diffusion time for sample B (10 times thicker than A crystals) had to be 100 times larger than that of sample A. This is in contradiction with the experimental result, that the diffusion time for sample B is only 6 times larger than that of sample A. This means that the oxygen out-diffusion takes place in the a - b planes. This is in agreement with the oxygen tracer diffusion result for Bi-2212, namely $D_{ab}/D_c = 10^4$ – 10^6 [11]. For a crystal of dimensions $a \times b \times c$, the in-plane diffusivity D_{ab} is given by

$$D_{ab} = [1/a^2 + 1/\alpha b^2 + 1/\beta c^2]^{-1}/\pi^2 t, \quad (2)$$

where α is the anisotropy ratio between D_a and D_b , and β is the anisotropy ratio between D_{ab} and D_c . Since β is about 10^4 – 10^6 , the third term in Eq. (2) may be neglected; then

$$D_{ab} = [1/a^2 + 1/\alpha b^2]^{-1}/\pi^2 t. \quad (3)$$

After substitution of the values for a , b , and t for sample A and B (the typical diffusion timescales are indicated in Fig. 4, for sample A and B, we get $\alpha \geq 5$ –6 and $D_{ab} \approx 6.12 \times 10^{-8}$ cm²/s at 500°C. It follows that the oxygen out-diffusion in the a - b plane is quite anisotropic as well and that it is mainly along the a -direction. From Fig. 3, we know that the sample will decompose when the annealing temperature in nitrogen is above 700°C. If the oxygen out-diffusion is mainly along the a -axis, a Bi-2212 single crystal of size $3 \times 1 \times 0.1$ mm³ annealed in nitrogen above 700°C is expected to show decomposition along the a -direction only. This kind of decomposition is indeed directly observed as is shown in Fig. 5. So, be-

Fig. 5. Decomposition of Bi-2212 single crystal (size $3 \times 1 \times 0.1$ mm³) along the *a*-direction after annealing in nitrogen above 700°C.

sides the sample geometry, the anisotropic-diffusion rate in the *a*-*b* plane should also be taken into account if effective diffusion lengths have to be computed. From Fig. 4, it clearly follows that there are at least two oxygen out-diffusion mechanisms involved. When *t* is smaller than 800 s, a fast mechanism of interstitial diffusion dominates; above 800 s, the other mechanism plays an important role, with a much longer diffusion time.

Finally, we want to study the different diffusion

Fig. 6. The weight change of sample B versus time at 500°C after a change of surrounding atmosphere from air to nitrogen and then from nitrogen to oxygen.

rates for oxygen out- and in-diffusion. As can be seen in Fig. 6, the timescales for isothermal oxygen out-diffusion in nitrogen and in-diffusion in oxygen at 500°C is quite different, the oxygen in-diffusion is much faster than the out-diffusion. This is consistent with the result of in-situ resistance measurements [6]. However, as can be seen in Fig. 6, the amount of oxygen change is not reversible. In addition, from AC susceptibility measurements we determined that T_c is almost reversible, but the X-ray diffraction analysis did not show complete reversibility. The reason is still not known. Therefore it may be important to point out that one should be careful with determining oxygen diffusion by means of an in-situ resistance measurement [6].

5. Conclusion

We have studied the weight change of Bi-2212 single-crystalline samples by a classical thermogravimetric technique. A plateau was observed in the dependence of T_c and the *c*-axis lattice parameter on the oxygen contents. Considering the sites of the oxygen loss, it is suggested that at least two sites in the structure are involved: the interstitial site (site A) between the Bi–O layers, and site B which we speculate to lie in the Cu–O layers. T_c and the *c*-axis lattice parameter do not depend on the amount of oxygen loss from site B. So the hole-carrier concentration in Bi-2212 may originate from the Bi–O reservoir, i.e. a self-doping mechanism. From the oxygen-diffusion studies, it was found that oxygen in-diffusion is much

faster than oxygen out-diffusion, but the amount of oxygen change is not reversible. The oxygen out-diffusion is quite anisotropic, mainly along the *a*-direction.

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