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EFFECT OF OXYGEN DEFICIENCY IN HIGH-T_C MATERIALS

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Abstract

It is well established that the superconducting and structural properties of $YBa_2Cu_3O_x$ depend markedly on the oxygen stoichiometry and vacancy ordering. By tuning the oxygen content, tetragonal and orthorhombic $YBa_2Cu_3O_x$ structural phases can be prepared. Changes in the oxygen content induce a metal - insulator transition and have a striking influence on the superconducting critical temperature, field and current. In the following, we will briefly review some effects of oxygen deficiency and vacancy ordering on the superconducting transport and magnetic properties of ceramic, single crystal and thin film $YBa_2Cu_3O_x$ superconductors.

1. Introduction

The oxygen concentration in high-T_c ceramics is one of the crucial parameters for the presence of high-temperature superconductivity.[1] Changes in the oxygen content induce structural transformations, metal-insulator transitions and variations in the onset temperature for magnetic and superconducting order. The oxygen kinetics of high-T_c copper-oxides is affected by the oxidation reaction as well as the oxygen diffusion processes.[2] Oxygen evolution techniques allow the identification of different desorption mechanisms present, and the detection of a variety of impurity phases.[3–6] These techniques can also be used to determine the oxygen stoichiometry of thin films.

2. Influence of the Oxygen Content on the Physical Properties

2.1. A variety of methods can be used for the preparation of oxygen deficient material.[2,7,8] Most methods are designed for the preparation of material in thermodynamic equilibrium,[9] which for fixed values of the oxygen pressure P_{O_2} and the temperature T, sets in after a time t_o. It should be noted however, that even in thermodynamic equilibrium, the material might be inhomogeneous, due to a different chemical potential present in the interior and surface of the grains. Using the P_{O_2} - T phase diagram for $YBa_2Cu_3O_x$ (Fig. 1), oxygen deficient samples with a fixed oxygen content, x, can be prepared in a reproducible and reversible way.

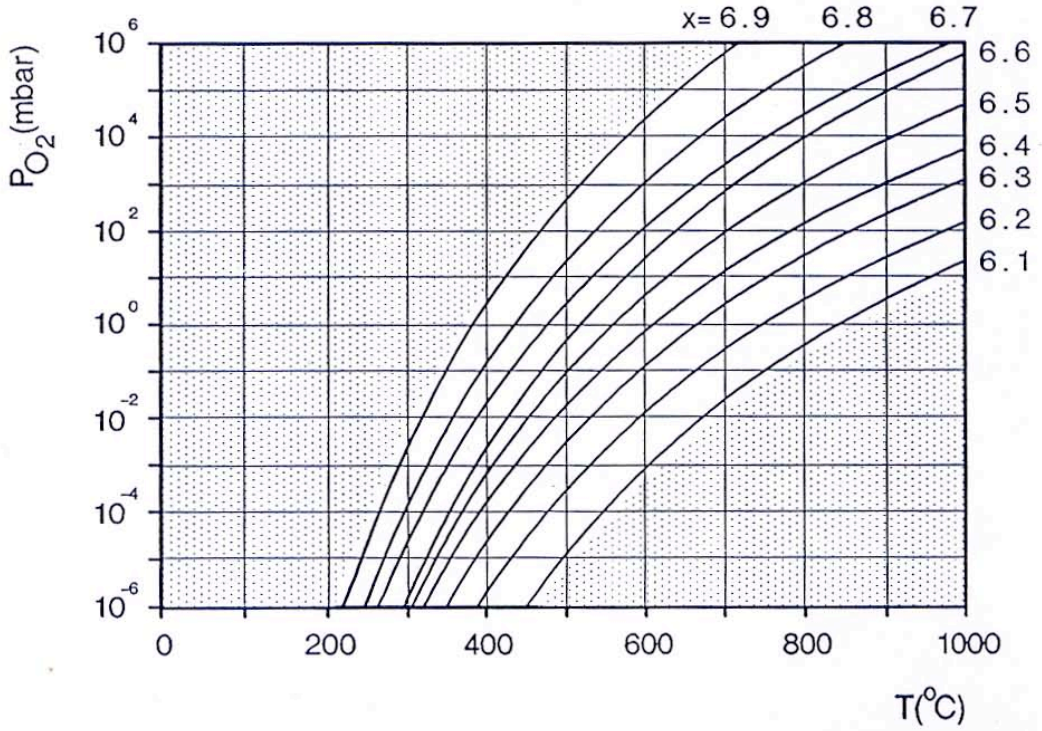

Figure 1. P_{O_2} - T diagram, derived from data of ref. 9, indicating for each temperature the oxygen partial pressure for which $YBa_2Cu_3O_x$ is stable (solid lines for different x values). The dotted areas on the left (x>6.9) and the right side (x<6.1) are the unstable regions.

The diagram was calculated from the results obtained by Gallagher[9] (solid curves). which were extrapolated to lower pressures. These curves delimit the region of thermodynamic stability for $YBa_2Cu_3O_x$ in the partial pressure-temperature phase space. Outside these regions, either secondary phases are formed or decomposition occurs.[10,11] The time to reach thermodynamic equilibrium is approximately 25 hrs at 400°C, and is shorter at higher temperatures. During cool down to room temperature the pressure should be changed so that the proper P_{O_2} - T conditions are present. At low pressure, it is safe to quench the samples, since the small amount of oxygen present will not change signif-

icantly the oxygen content of the sample. At higher pressures however, a quench from a temperature above 250°C can change the oxygen concentration at the sample and/or grain boundaries, and therefore induce inhomogeneities.

Figure 2 shows the temperature derivative of the RF-susceptibility for samples annealed for various lengths of time at 400°C.[12] The frequency shift of an oscillating (32MHz) RLC-circuit, which is directly proportional to the RF-susceptibility, is measured and enables to detect the superconducting phases present. The superconductivity is signaled by a sharp peak starting at 92 K for samples annealed less than 1 hr at 400°C. Between 2 hrs and 8 hrs anneal time, there is clear evidence for the presence of two superconducting phases : one at ~90 K and another at ~60 K. The straightforward implication of this data is that there are two distinct superconducting phases perhaps induced by different oxygen orderings. However, the unlikely possibility that this data is caused by grain size inhomogeneities in the sample can not be ruled out. Small grains will produce the low temperature "60 K" phase because they are quickly depleted of oxygen, whereas in the larger grains T_c will continuously change from 90 K to 60 K. In samples with uniform grain size one may expect only one phase in the thermodynamic equilibrium. Although it is not clear by all means, what the reason is for the presence of only two distinct sized grains.

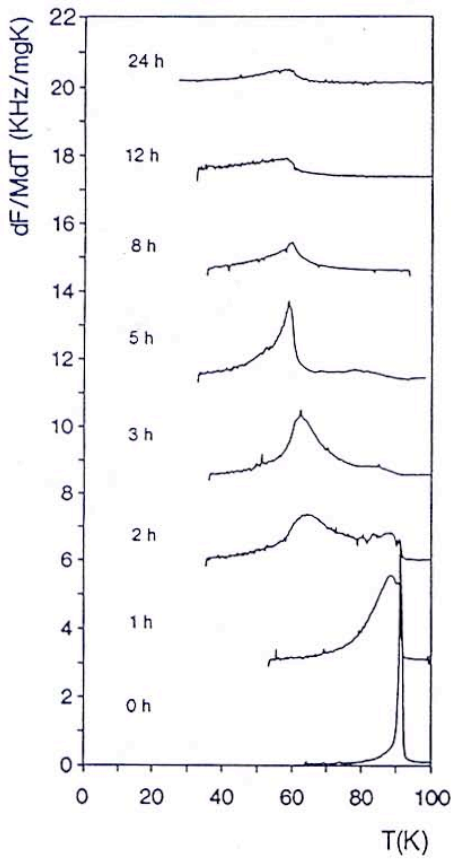

Figure 2. Normalized (with respect to the mass M) temperature derivative of the oscillator frequency F versus temperature, measured using an RF susceptometer, for a set of $YBa_2Cu_3O_x$ samples after different annealing times at 400°C. Curves are shifted upwards for clarity.

2.2. As indicated in the previous section, the oxygen content can be modified in a reversible way, which implies that the superconducting transition temperature which depends on the oxygen content can be tuned continuously. Many experiments have found that the exact shape of the T_c versus oxygen content (x) curve in $YBa_2Cu_3O_x$, is strongly affected by the material preparation conditions. In general it is concluded that T_c versus x exhibits a plateau around 60 K, when the oxygen is "gently" removed via out-diffusion at low temperature ($T \leq 400°C$).[13–15] On the other hand, a more monotonous decrease of T_c (plateau is less pronounced or completely absent) is observed when the oxygen is removed abruptly by quenching the sample from higher temperature.[16,17] A typical example of the two types of behaviour is shown in Fig. 3 (from ref. 17), where T_c is defined as the mid-point of the main superconducting transition. For the quenched samples (open circles), the T_c values were obtained from the resistive transition. For the "gently" treated samples, T_c was determined from resistive measurements (full circles) as well as from the Meissner signal (full squares). In order to define clearly the superconducting properties of a given sample, the results of resistive and inductive measurements should be combined. The resistive transition is determined by the percolating infinite clusters having the highest T_c; the measurement of the Meissner fraction in most cases provides information about the relative importance of the various phases with a different T_c.

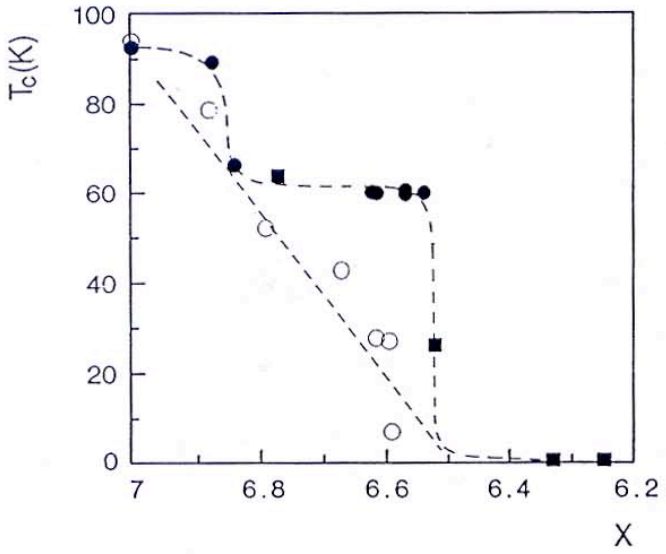

Figure 3. Critical temperature versus oxygen content in $YBa_2Cu_3O_x$, after ref. 17.

3. Implications for Thin Film Technology

3.1. The desorption spectra (x = number of evolved oxygen atoms per unit cell) for a single crystal ($\approx$ 2x1x1 mm^3). a polycrystalline pellet ($\approx$ 2 mg) and a thin film ($4x4x10^{-3}$ mm^3) of $YBa_2Cu_3O_x$, are shown in Fig. 4. These spectra were obtained using a gas evolution technique [3–6] in which a sample is placed in an evacuated quartz tube and heated at a constant rate ($\simeq$ 10°C/min) up to 950°C. During the heating process the pressure in the tube is monitored using a sensitive capacitance manometer and (or) a quadrupole

mass spectrometer. A typical desorption spectrum, e.g. for the ceramic sample (middle curve in Fig. 4), exhibits a clear peak around 600°C, and several sharp peaks around 800°C. The 600°C-peak corresponds to oxygen evolved from the Cu-O chains (O5-O1 position), while the high-temperature peaks indicate partial decomposition of the ceramic material.[5] For the thin film, the Cu-O chains apparently start to loose oxygen at a much lower temperature (380°C) when compared to the ceramic pellet or the single crystal. This shift is probably due to the difference in activation energy for oxygen evolution in the three systems. Indeed, the effective activation energy is determined by site to site hopping within the grains, diffusion along the grain boundaries caused by different chemical potentials, and also by desorption from the sample surface. For thin films it is clear that surface desorption enables the oxygen to evolve at lower temperatures. Moreover, the surface to volume ratio apparently determines the temperature at which the chains are depleted from oxygen.

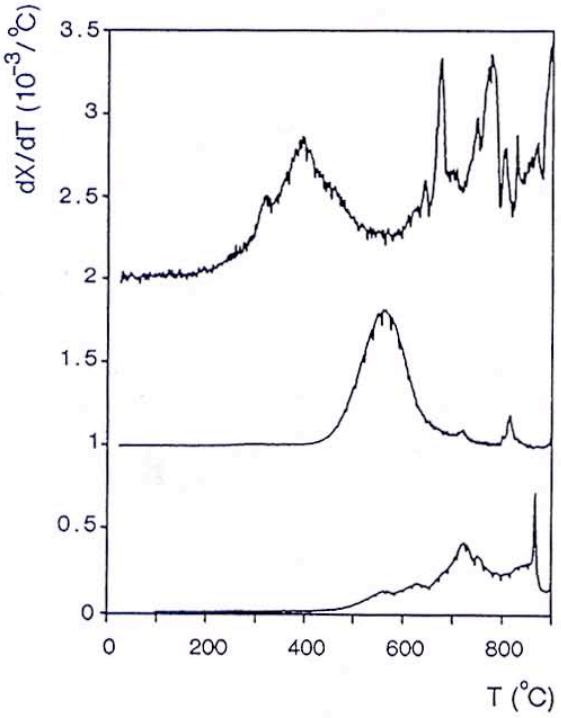

Figure 4. Oxygen evolution curves (shifted upwards for clarity) for a thin film (upper curve), a ceramic pellet (middle curve) and a single crystal (lower curve) of $YBa_2Cu_3O_x$.

3.2. In the framework of high-T_c thin film research, much attention has been paid to the interaction between the substrate and the deposited thin film. [18] The influence of the oxygen content on the properties of the substrates themselves has, to our knowledge, not been addressed.

Concentrating on one of the most commonly used substrates, $SrTiO_3$, we observed a very strong dependence of the substrate resistivity on the oxygen content, in accordance with the results published in 1964 by Frederikse et al.[19] Annealing studies on $SrTiO_3$ (100)

oriented samples at high temperatures were performed in the ultrahigh vacuum evolution system described above. Oxygen evolves at 800°C in a reduced atmosphere of 10^{-6} Torr. Low temperature resistivity measurements were performed on these reduced samples using the standard four probe technique. Figure 5 shows the temperature dependence of the resistivity for vacuum annealed (P_{O_2} = 5x10^{-8} Torr) $SrTiO_3$ at 850°C during 1 hr, at 1050°C during 1 hr, and at 950°C during 1 minute only. The two lower curves show the behaviour of the samples annealed during a longer time. The dotted, and dashed lines indicate annealing at 850°C and 1050°C respectively. From these measurements, it is clear that $SrTiO_{3-y}$ becomes metallic. When comparing these data with those obtained for thin film ceramic superconductors on $SrTiO_3$, it should be remembered that the thickness of substrate and thin film are different. Although the resistivity of the $SrTiO_3$ is quite high, its resistance may be comparable to that of the thin film. This is shown in Fig. 6, where the resistance of the $SrTiO_3$ substrate annealed at 950°C in a pressure P_{O_2} = 5x10^{-8} Torr, is compared with the resistance versus temperature variation obtained for a 500 nm thin $YBa_2Cu_3O_x$ film, prepared by single target magnetron sputtering on a YSZ substrate (surface of 5x5 mm^2). We should also mention that $SrTiO_3$ is diamagnetic, before as well as after the oxygen evolution. These results indicate that caution should be exercised in interpreting resistivity and susceptibility data of high-temperature superconducting thin films deposited on $SrTiO_3$ substrates.

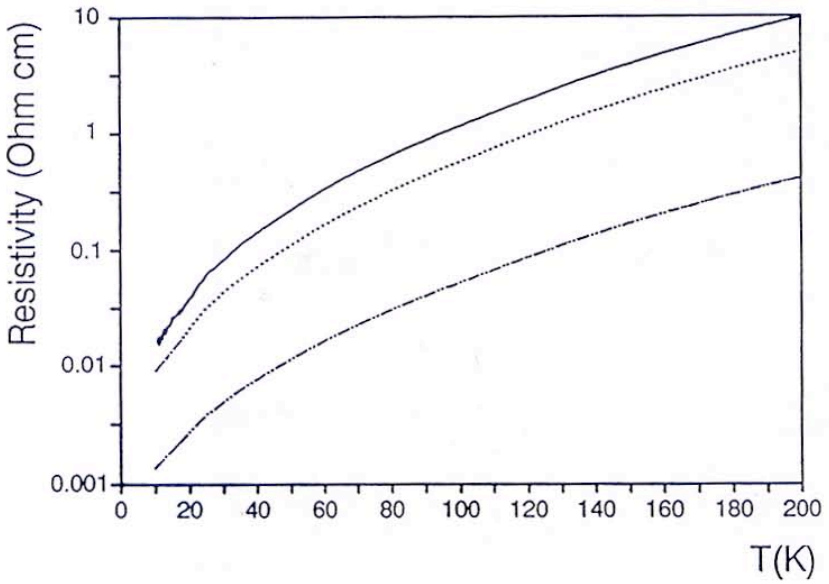

Figure 5. Temperature dependence of the resistivity for oxygen deficient $SrTiO_3$ for substrates annealed at different temperatures in P_{O_2} = 5x10^{-8} Torr. (−−) 950°C during 1 minute; (· · ·) 850°C during 1 hr; (− · −) 1050°C during 1 hr.

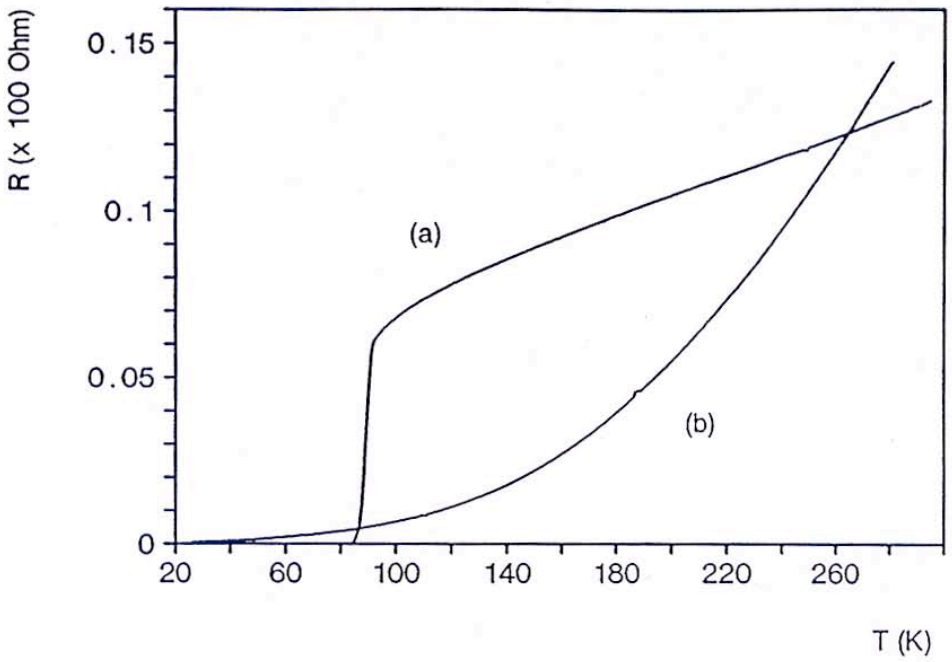

Figure 6. Temperature dependence of the resistance of a thin $YBa_2Cu_3O_x$ film on YSZ (a) and of an oxygen deficient $SrTiO_3$ substrate (b) with the same area.

4. Conclusions

Gas evolution is a powerful technique for the study of oxygen stoichiometry and thermodynamics in ceramic superconductors. The use of this technique allows the reproducible preparation of oxygen deficient single crystal, ceramic and thin film superconductors. The oxygen evolution in $YBa_2Cu_3O_x$ is characterized by a low temperature oxygen evolution peak from the O1 and O5 sites and several high temperature peaks which are associated with impurity phases and decomposition. The exact shape and position of the evolution curve depends in a complicated way on the mechanisms which control the oxygen kinetics. High temperature ceramic oxides containing one ore two distinct superconducting phases can be prepared by performing long time, moderately low temperature (400°C) anneals. These type of anneals result in gradual changes in the oxygen volume fraction of the superconducting phases without major shifts in their transition temperatures. These annealing studies seem to imply the presence of two distinct oxygen phases although the accidental presence of reproducible inhomogeneities in a large number of samples can not be ruled out. Gas evolution studies on $SrTiO_3$ (a commonly used substrate material) show that oxygen depletion causes it to become metallic. This together with the diamagnetism present in $SrTiO_3$ must be taken into account when thin film superconductivity data on $SrTiO_3$ are interpreted.

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