

## OXYGEN STOICHIOMETRY AND SUPERCONDUCTIVITY IN CERAMICS

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### ABSTRACT

We have performed extensive gas evolution, X-ray diffraction and superconducting measurements on a series of high temperature ceramics as a function of oxygen composition. Constant rate gas evolution studies allow a unique identification of the oxygens evolving from the various inequivalent sites and permit a determination of their activation energies and frequency factors. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  the evolution kinetics at fixed temperature and varying lengths of time is found to proceed by an initial large change in chain occupancy and a subsequent leveling off. The transition temperature determined from high frequency susceptibility measurements follows this behavior; a fast decrease in  $T_c$  up to a plateau around 60 K. The volume fraction of superconducting material decreases steadily, until the sample becomes non-superconducting.

### INTRODUCTION

It is by now clearly established that changes in oxygen content can strongly affect the properties of high temperature ceramic superconductors. However, to date no clear cut picture has emerged which establishes uniquely the role of oxygen ordering, orthorhombicity, oxygen stoichiometry and their relationship to the superconducting properties.<sup>1</sup> The main reasons for these difficulties are that it is hard or perhaps impossible to determine in a unique way the presence of more than one oxygen phase. The establishment of oxygen ordering requires the application of complicated structural probes and in many cases the properties seem to depend delicately on a variety of preparation conditions.

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For the past two years we have embarked on a program dedicated to answering some of these questions. In this program, we have applied powder metallurgy and thin film techniques to prepare samples, x-ray and neutron diffraction together with gas evolution to establish the structure and stoichiometry and resistivity, magnetisation and high frequency susceptibility to study the superconducting properties.<sup>2,3</sup> These studies show that due to the complexity of the problem extensive systematic studies are needed in order to establish the general phenomenology of oxygen ordering in ceramics. In order to address these problems we have restricted our attention to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and substitutions since this system is well understood structurally, much of its general phenomenology has been studied by a number of groups and it contains all interesting structural features, such as copper- oxygen chains and planes.

#### DETERMINATION OF OXYGEN STOICHIOMETRY

All detailed structural determinations done to date, especially the Rietveld refinements of neutron data, show consistently disagreements between calculation and experiment in certain ranges of k-vector.<sup>4</sup> The disagreements always occur in the same k-vector ranges and have the same character indicating that these are not due to subtle differences in the various samples but are possibly due to real structural inaccuracies, possibly due to a number of distinct oxygen phases. Unfortunately, neutron diffraction has not been able to establish the presence of various phases with different oxygen stoichiometry.<sup>5</sup>

We have applied a gas evolution technique, previously used to study hydrogen kinetics in amorphous silicon,<sup>6</sup> to study oxygen bonding in high temperature superconducting ceramics. These type of measurements allow a quantitative determination of oxygens in sites which have distinct binding energies. This measurement is complimentary to the traditional thermogravimetric measurement and it also allows the determination of oxygen binding energies.<sup>7</sup>

The sample (10 - 30 mg) is placed in an evacuated quartz tube. The temperature is then raised at a constant rate (typically 10°C/min) and the pressure in the vessel is measured with a pressure gauge and analysed using a quadrupole mass spectrometer. The data are then corrected with the experimentally determined evolution from an empty tube. All corrections amount to less than 5 % . The number of evolved oxygen atoms is directly related to the time derivative of the pressure if a constant heating rate is applied.

Figure 1 shows a comparison of gas evolution from a number of high temperature superconductors. Note that the samples which contain Cu-O chains in their structure ( $\text{LaBa}_2\text{Cu}_3\text{O}_{7+\delta}$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $\text{Y}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ) exhibit an evolution peak centered around 600°C. A further comparison of this data with neutron scattering measurements clearly indicates that this peak corresponds to evolution from the Cu-O chains.<sup>8</sup> A binding energy of 1.2 eV is obtained from a fit assuming first order desorption, the broad width of the evolution peak arising possibly from the presence of various inequivalent sites. The high temperature peak cannot be uniquely identified, although it is thought that they arise from impurity phases and/or decomposition.

The oxygen desorption kinetics can be studied using this methodology very conveniently. In order to allow for proper ordering of the oxygens, low temperature ( $400^{\circ}\text{C}$ ), long time (0 - 100 hrs) anneals have been performed possibly while the sample is in the tetragonal phase.<sup>9</sup>

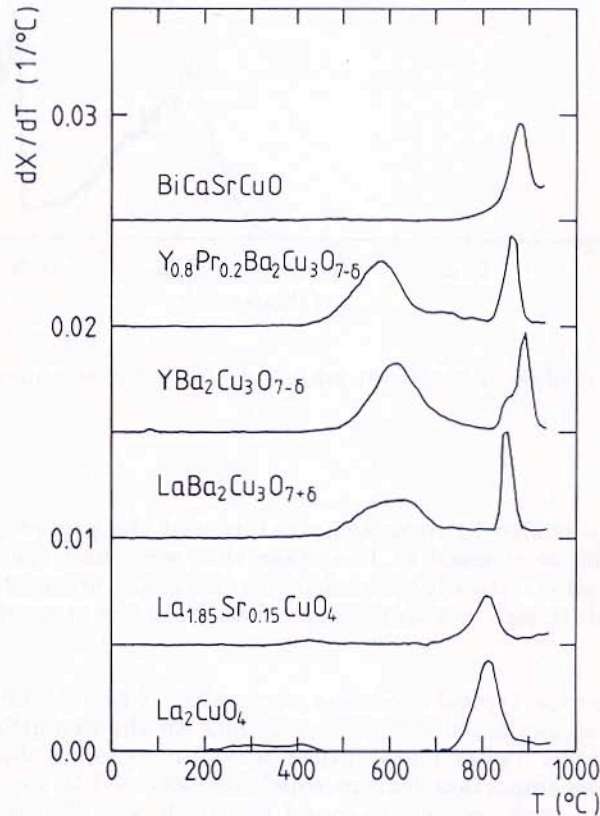


Fig. 1. Temperature derivative of the number of oxygen atoms evolving from different ceramic superconductors. (Curves are shifted upwards for clarity)

To avoid questions related to sample inhomogeneity one single sample was repeatedly heated for various lengths of times at  $400^{\circ}\text{C}$  in vacuum. After each annealing cycle the sample was slowly ( $100^{\circ}\text{C/hr}$ ) cooled to room temperature. Then the magnetic susceptibility was measured in cooling and heating from 300 K to 20 K. Once the superconducting properties were measured gas evolutions as described earlier were performed up to  $950^{\circ}\text{C}$ . Consequently, the

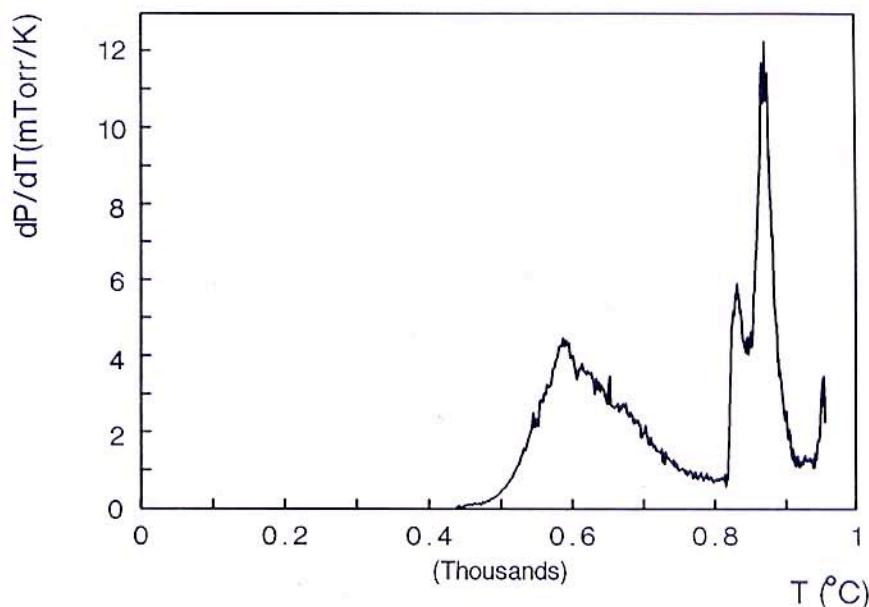


Fig. 2. Typical evolution spectrum for a sample that was annealed at 400°C for 3 hours.

sample was slow cooled to room temperature and the process was repeated again. It should be stressed at this stage that we found that the physical properties are quite critically dependent on the exact process, i.e. vacuum, anneal temperature etc., possibly due to changes in the structure during annealing.

Figure 2 shows a typical evolution curve after 3 hrs of anneal at 400°C. The first peak as explained earlier corresponds to the evolution from Cu-O chains, whereas the higher temperature peaks are possibly due to impurity phases. The most important feature which is connected to the superconductivity is the first peak, centered around 600°C. It was shown very early in the field of high temperature superconductors that the oxygen content and/or ordering of the Cu-O chains are correlated critically with the superconducting properties.<sup>10,11</sup>

Figure 3 shows the oxygen loss in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  under the lower (600°C) peak as a function of anneal time at 400°C. The evolution is characterized by a fast decrease in oxygen concentration in the first few hours of anneal followed by a plateau which is constant up to 100 hrs.

The difference in the oxygen kinetics at 400°C can be understood in light of the oxygen thermodynamics. The heat of solution of oxygen has a very strong dependence on the overall oxygen concentration. At high concentrations the

heat of solution is small and therefore the oxygen is desorbed readily, at low concentrations the heat of solution is higher and therefore the desorption becomes very difficult in accordance with the results shown in Fig. 3.

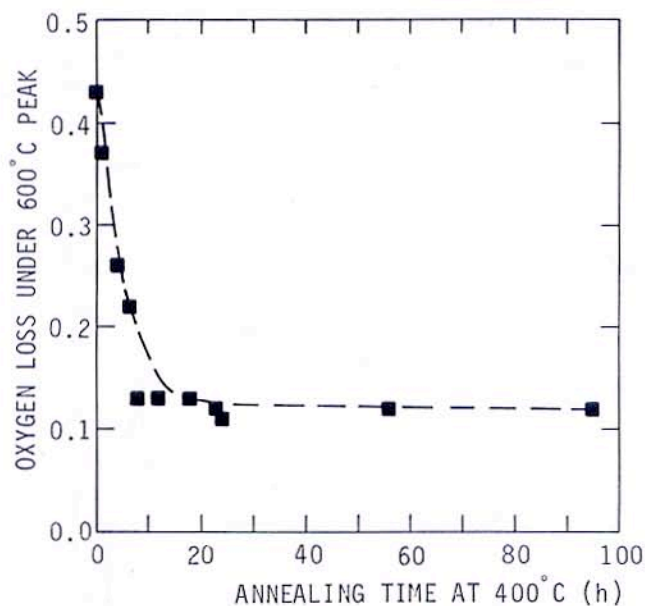


Fig. 3. Evolution of the O1 and O5 ("chains") occupancy versus annealing time at 400°C.

### SUPERCONDUCTIVITY

The correlation of the superconducting properties with the gas evolution has been performed by measuring the high-frequency (32 MHz) susceptibility obtained from the frequency change of an RLC oscillator containing the sample. The superconducting transition is signaled by a sharp step in the susceptibility versus temperature curve. The normalized temperature derivative of this curve allows a precise determination of the onset, midpoint and completion of the superconducting transition. The area under the derivative curve is proportional to the volume fraction of the superconducting phase present.

Figure 4 shows a series of derivative curves for various annealing times. There is a systematic fast decrease of the transition temperature from 90 K to

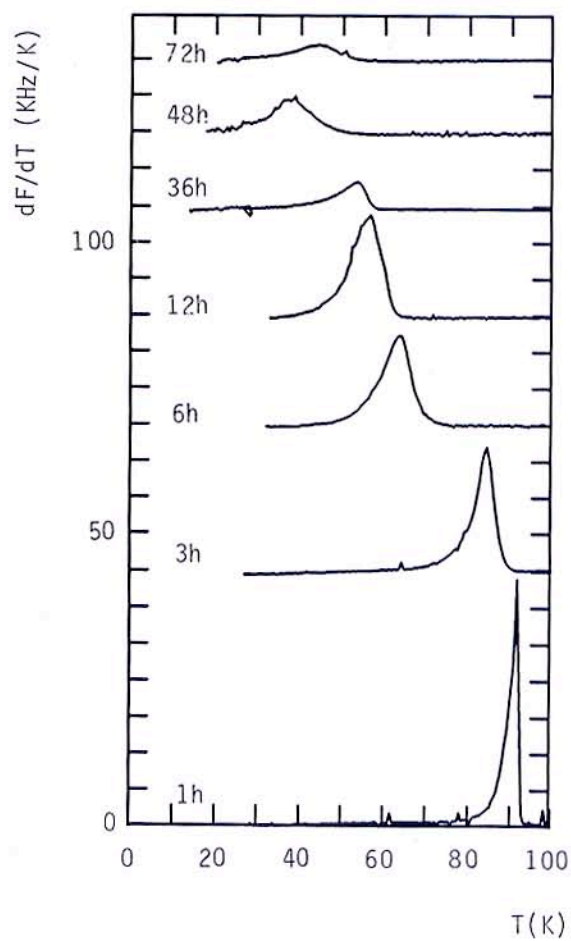


Fig. 4. Frequency change of the RLC oscillator circuit (proportional to the susceptibility change) versus temperature for samples with different annealing times at 400°C. (Curves are shifted upwards for clarity)

55 - 60 K and then  $T_c$  levels off (Fig. 5). Clearly this  $T_c$  behavior is correlated with the oxygen evolution curves (Fig. 3). The width of the transition from the normal to the superconducting state does not change considerably along the  $T_c$  versus annealing time curve (Fig. 4). On the  $T_c$  plateau, however, the volume fraction of the "60 K phase" decreases progressively for longer annealing times (Fig. 4). It should be pointed out that in some samples a two phase behavior was observed with the 90 K phase persisting for some annealing time. The details of this two phase behavior are presently under investigation.

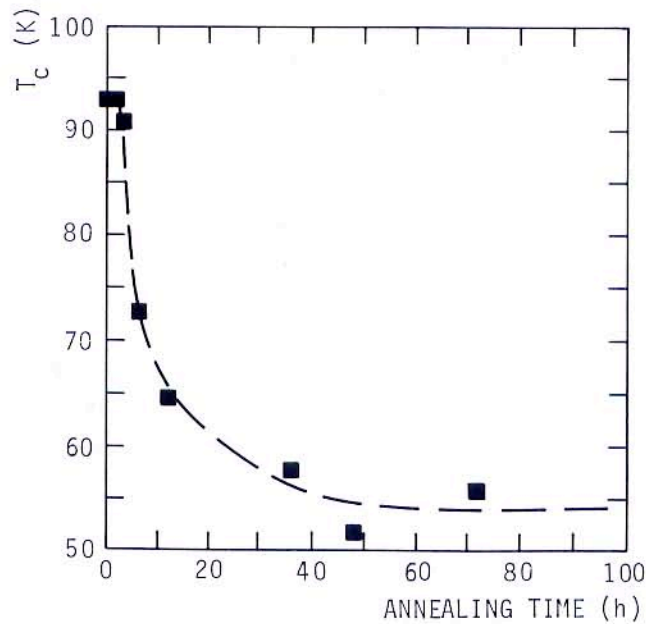


Fig. 5. Evolution of the transition temperature  $T_c$  versus annealing time at 400°C.

These results indicate that as the oxygen deficiency increases, a phase with an intermediate  $T_c$  between 90 and 60 K is formed. Further anneal of this phase, although it doesn't change the total oxygen stoichiometry, decreases the volume fraction of the phase. At some point percolation is lost and in a resistive measurement for instance the sample becomes normal.

In summary, we have shown that in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  long time anneals at  $400^\circ\text{C}$  produce samples with  $T_c$ 's in the range 90 - 55 K. The kinetics proceeds by a fast decrease in oxygen concentration followed by a plateau which persists for anneals up to 100 hrs. The superconducting transition temperature follows this behavior, a fast decrease in  $T_c$  followed by a plateau around 55 - 60 K. Along the plateau however, the volume fraction of superconducting material decreases steadily, until the sample becomes nonsuperconducting.

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