# THE EFFECTS OF OXYGEN STOICHIOMETRY AND OXYGEN ORDERING ON SUPERCONDUCTIVITY IN $Y_1Ba_2Cu_3O_{9-x}$

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## ABSTRACT

This paper reports on the structures and properties of $Y_1Ba_2Cu_3O_{9-x}$ samples prepared in precisely controlled oxygen environments using a solid-state ionic technique. By titrating out oxygen at low temperatures, orthorhombic $Y_1Ba_2Cu_3O_{9-x}$ samples were prepared with oxygen contents below 6.50. Resistivity and magnetometry studies indicated that these reduced, orthorhombic samples were marginally superconducting, with their superconductivity probably arising from local regions of higher oxygen content.

## INTRODUCTION

Early on, it was recognized that the properties of oxide superconductors depend critically on processing conditions [1]. Using a variety of characterization techniques, numerous groups reached qualitatively similar conclusions regarding the importance of controlling the oxygen content and oxygen order for optimal superconducting properties. Quantitatively, however, the results of different groups vary considerably. For example, Johnston *et al.* [2] found samples prepared by interdiffusing mixtures of $Y_1Ba_2Cu_3O_6$ and $Y_1Ba_2Cu_3O_7$ in sealed silica tubes to be tetragonal and not superconducting below $Y_1Ba_2Cu_3O_{6.5}$, whereas Cava *et al.* [3] found samples prepared by a zirconium gettering technique to be orthorhombic with a large superconducting volume fraction at $Y_1Ba_2Cu_3O_{6.30}$. One cause for these discrepancies is that the techniques used to prepare oxide samples thus far do not allow for precise control of all of the important processing variables — namely, the annealing temperature, oxygen partial pressure, and quench rate [4]. Herein, we describe a solid-state ionic method for preparing oxide samples with well-defined processing histories. Using this method, we have prepared and examined $Y_1Ba_2Cu_3O_{9-x}$ samples with oxygen contents at and below 6.50.

## EXPERIMENT

The solid-state ionic cell used consisted of a closed quartz jacket with two interconnected chambers, as shown schematically in Fig. 1. Each chamber had its own furnace for independent temperature control. One chamber contained the $Y_1Ba_2Cu_3O_{9-x}$ sample. A nearby thermocouple monitored the thermal history of the sample, including the quenching process. The other chamber housed a yttria-stabilized-zirconia (YSZ) solid electrolyte tube, closed at one end, with porous platinum electrodes deposited on the inner and outer walls at the closed end. The interior of the YSZ tube was exposed to ambient air, to act as an oxygen reference electrode.

The YSZ tube served two purposes. First, passing a known current through the electrolyte allowed quantitative titration of oxygen into and out of the chamber. Second, measuring the open circuit voltage across the electrolyte enabled the oxygen partial pressure inside the chamber to be accurately measured. The YSZ tube chamber was operated at a fixed temperature of 850 °C to obtain high ionic conductivity and thus rapid oxygen transport.

Samples with reduced oxygen content were prepared in the following manner. $Y_1Ba_2Cu_3O_{7.00}$ starting material (oxygen content derived from iodometric titration [5]) was placed in an alumina boat in the chamber and heated to 500°C. During the temperature ramp up, enough oxygen was pumped out of the chamber to ensure that the total pressure remained below 1 atm. At 500 °C, oxygen was titrated out of the chamber for 2 - 3 days. The sample remained

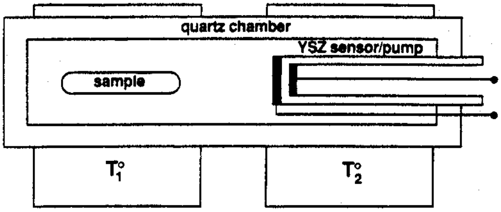

Figure 1. Schematic of the apparatus.

at 500 °C for an additional day after the desired oxygen content was attained. The sample was then either air quenched to 25 °C by removing the furnace around the sample compartment or slowly cooled by stepping down the sample furnace temperature to 25 °C over a 28 hour period:

The oxygen content in the reduced samples was derived from the known starting composition and the measured weight change in the sample (total sample weight ~10 grams). This value was checked by performing thermogravimetric analysis and iodometric titration on small portions of each sample. Based on the results of these three methods, we estimate that the quoted oxygen contents are accurate to within ±0.02 oxygens per formula unit.

X-ray diffraction and transmission electron microscopy (TEM) were used for structural characterization of the samples. Resistivity, thermopower, and susceptibility measurements were used to determine corresponding changes in superconducting properties.

## RESULTS

The x-ray diffraction patterns, resistivity versus temperature plots, and diamagnetic shielding data for samples air quenched from 500°C with oxygen contents between 6.30 and 6.50 are shown in Figs. 2, 3, and 4, respectively.

### Air quenched $Y_1Ba_2Cu_3O_{6.30}$

X-ray diffraction indicated that the $Y_1Ba_2Cu_3O_{6.30}$ sample was tetragonal [Fig. 2(a)]. Electron diffraction studies of individual crystals also found the material to be tetragonal. No twins were observed in the microstructure, as expected for tetragonal crystals. A few crystals, however, did exhibit a feint, tweed-like microstructure, as if on the verge of transforming to the orthorhombic structure. Resistively, the sample never went superconducting [Fig. 3(a)]. Magnetometry data, however, indicated approximately 0.2% of the sample was superconducting below ~30 K (Fig.4).

### Air quenched $Y_1Ba_2Cu_3O_{6.41}$

Both x-ray and electron diffraction indicated that the $Y_1Ba_2Cu_3O_{6.41}$ sample was orthorhombic. Moreover, the electron diffraction patterns exhibited weak superlattice spots halfway between reflections along the a* axis, corresponding to a doubling of the a axis in the unit cell. Similar spots along the b* axis have been reported by Cava *et al.* in $Y_1Ba_2Cu_3O_{6.72}$ samples [3]. The twin density in this sample was similar to that in $Y_1Ba_2Cu_3O_{7.00}$ material. Dips occurred at 80, 50, and 30 K in the resistivity data [arrowed in Fig. 3(b), see below]. The sample did not reach zero resistance until 4 K. Diamagnetic shielding in the sample was only 2% of that expected for a perfect diamagnet, indicating that most of the sample was not superconducting (Fig. 4).

### Air quenched $Y_1Ba_2Cu_3O_{6.50}$

The diffraction studies indicated that the orthorhombic distortion in this sample was greater than that in the $Y_1Ba_2Cu_3O_{6.41}$ sample, as expected [Fig. 3(c)]. Thermopower, resistivity, and susceptibility measurements all found a $T_c$ of 37 K for this sample. The diamagnetic shielding in this sample was about 20% of that expected for a perfect diamanget (Fig. 4).

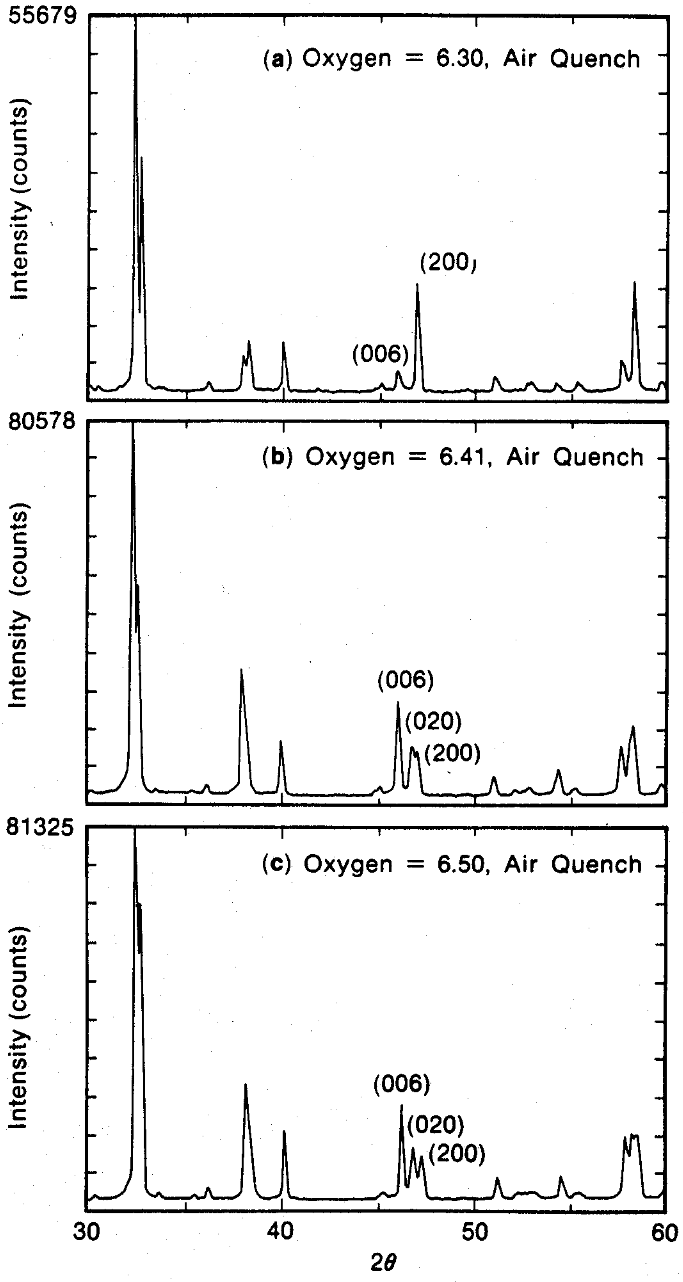

Figure 2. X-ray diffraction patterns for samples air quenched from 500°C with oxygen contents of (a) 6.30, (b) 6.41, and (c) 6.50.

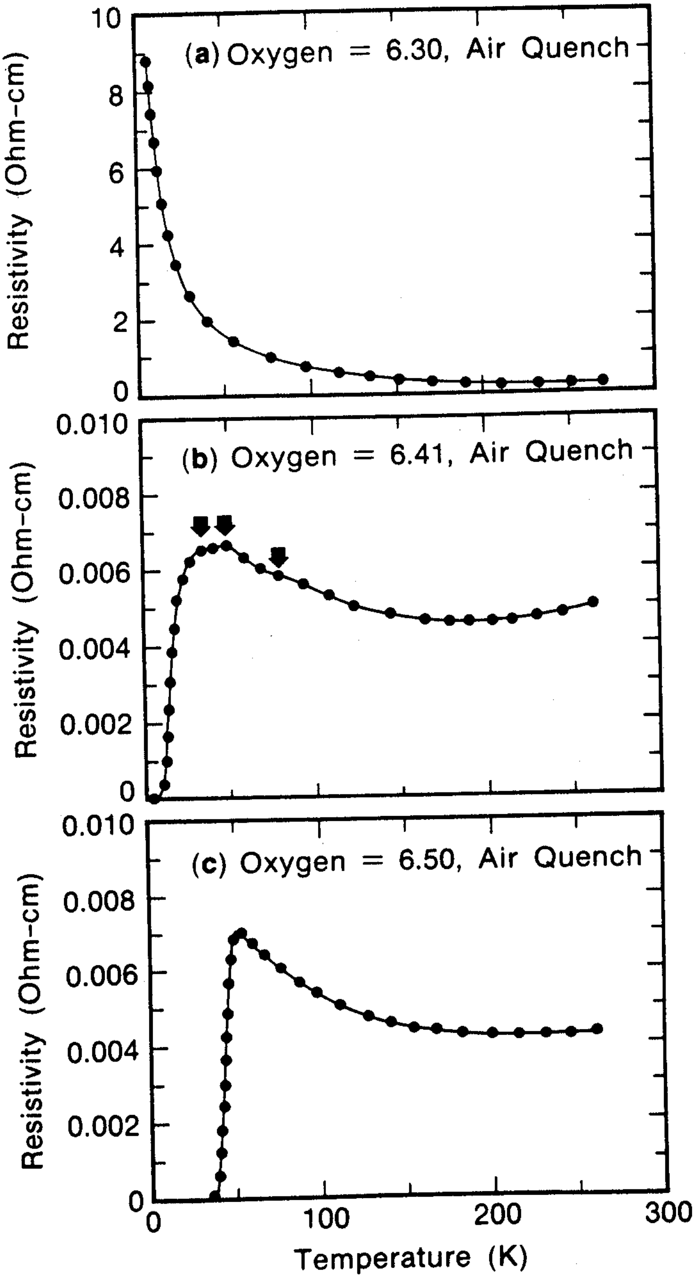

Figure 3. Resistivity versus temperature plots for samples air quenched from 500°C with oxygen contents of (a) 6.30, (b) 6.41, and (c) 6.50.

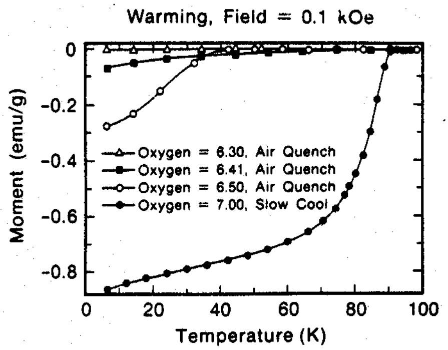

Figure 4. Diamagnetic shielding data for air quenched, reduced oxygen content $Y_1Ba_2Cu_3O_{9-x}$ samples and slowly cooled $Y_1Ba_2Cu_3O_{7.00}$ starting material.

### Slow cooled $Y_1Ba_2Cu_3O_{6.41}$

The x-ray diffraction pattern and resistivity versus temperature plot for a $Y_1Ba_2Cu_3O_{6.41}$ sample that was slowly cooled from 500 °C to 25 °C over a 28 hour period are shown in Fig. 5. The (200) and (020) diffraction peaks are sharper and more clearly separated than those in the air quenched $Y_1Ba_2Cu_3O_{6.41}$ sample [compare Figs. 5(a) and 2(b)], indicating greater oxygen ordering in the slowly cooled sample. (This conclusion is currently being checked with neutron diffraction.)

Both resistivity and susceptibility measurements, however, indicated that the slowly cooled material had a lower transition temperature than the air quenched material. The slowly cooled sample had a higher resistivity over the entire temperature range studied and it did not reach zero resistance down to 4 K [Fig 5(b)]. Figure 6 compares the shielding data in the two samples. (Note the vertical scale is greatly expanded compared to Fig. 4.) The air quenched sample contained regions that were superconducting up to 80 K. We interpret the slope changes in both the shielding and resistivity data of the air quenched sample [Figs. 6 and 2(b)] as evidence for local regions in the material with critical temperatures of 30, 50, and 80 K. It is reasonable to suggest that local inhomogeneities in the oxygen content of this sample gave rise to these superconducting regions. We are currently investigating whether these inhomogeneities arose from insufficient equilibration time at 500 °C or were caused by stress induced diffusion during the quench. By comparison, the shielding data for the slowly cooled sample indicated only trace amounts of material with a critical temperature of 50 K (not observable in Fig. 6) and somewhat larger regions with a critical temperature of 10 K (arrowed in Fig. 6).

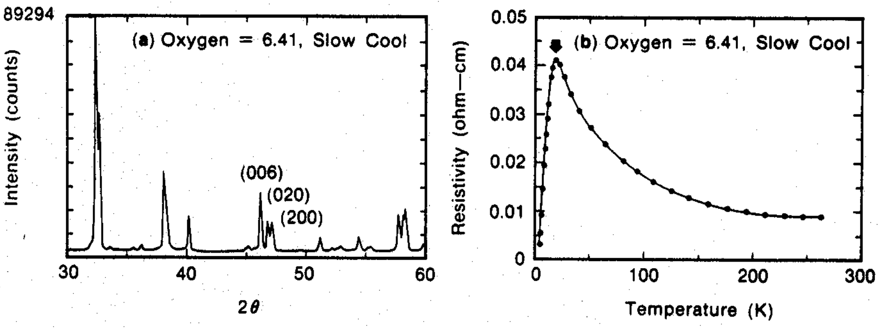

Figure 5. (a) X-ray diffraction pattern and (b) resistivity versus temperature plot for a slowly cooled $Y_1Ba_2Cu_3O_{6.41}$ sample.

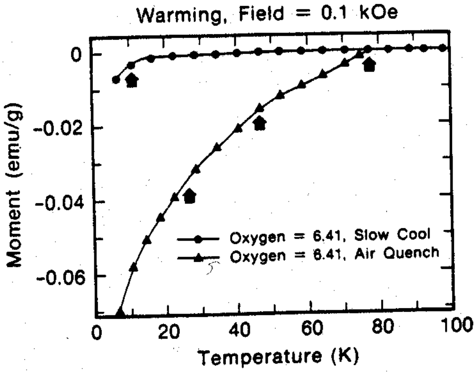

Figure 6. Enlarged plot of shielding data for slow cooled $Y_1Ba_2Cu_3O_{6.41}$ and air quenched $Y_1Ba_2Cu_3O_{6.41}$ samples. The arrows point out slope changes. Corresponding slope changes in the resistivity data are arrowed in Figs. 2(b) and 5(a).

## CONCLUSIONS

(1) Like Cava *et al.* [3], we find that orthorhombic $Y_1Ba_2Cu_3O_{9-x}$ material with oxygen content below 6.5 can be prepared by low-temperature removal of oxygen from $Y_1Ba_2Cu_3O_{7.00}$. For oxygen removal at 500 °C, however, we find that the orthorhombic phase cannot be retained down to $Y_1Ba_2Cu_3O_{6.30}$. Lower titration temperatures may extend the oxygen stoichiometry range of the orthorhombic phase.

(2) Our results indicate that oxygen inhomogeneities are essential for observing small amounts of superconductivity in $Y_1Ba_2Cu_3O_{9-x}$ samples with oxygen contents below 6.5. This conclusion supports the view that a high oxidation state in the copper-oxygen network, whether on a local scale (inhomogeneities in $Y_1Ba_2Cu_3O_{<6.5}$ samples) or on a global scale ($Y_1Ba_2Cu_3O_{>6.5}$ samples), is essential for high-temperature superconductivity.

(3) The solid-state ionic method described here enables complete control of both the thermal history of the sample and its oxygen environment. It can be readily used for well-defined studies of other oxide samples of interest, including single crystals, thin films, and the many $(R.E._xY_{1-x})(A_yBa_{2-y})(B_zCu_{3-z})O_{9-\delta}$ -type derivatives that have been made. Moreover, the same apparatus can be used for quantitative studies of phase equilibria in these oxide systems[6].

## ACKNOWLEDGEMENTS

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