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Probing oxygen ordering in YBCO by *in situ* high temperature resistivity and X-ray diffraction studies

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Abstract. In the high temperature superconducting material yttrium barium copper oxide (YBCO) the basal plane oxygen plays a dominant role in determining the superconducting properties of the material. We have carried out *in situ* high temperature measurements of (a) electrical resistivity and (b) X-ray diffraction in vacuum as well as in helium atmospheres to probe the nature of ordering of oxygen atoms. While published phase diagram of temperature vs oxygen concentration in different partial pressures allow only a tetragonal phase for the annealing temperatures we have investigated, the experiments point to the coexistence of orthorhombic (OII) and tetragonal phases.

Keywords. Oxygen order; XRD; resistivity.

1. Introduction

In the high T_c material $Y_1 Ba_2 Cu_3 O_{6+x}$, it is well known that the superconducting and normal state properties depend both on x and on the ordering of oxygen atoms in the basal plane. Several observations (Van Tandeloo *et al* 1987; Alario-Franco *et al* 1988; Beyer *et al* 1988) exist of ordered domains in microscopic regions by electron diffraction. But there is as yet no report of observation of ordering on a macroscopic scale. To understand the conditions for obtaining macroscopic regions of ordered domains we have carried out *in situ* electrical resistance measurements and *in situ* X-ray diffraction (XRD) studies at high temperatures in samples subjected to specified heat treatments in vacuum/helium atmosphere. The high temperature electrical resistivity measurements were carried out using a specially designed apparatus (Narasimha Rao *et al* 1996). *In situ* high temperature XRD studies were carried out in (a) vacuum of 10^{-4} Pa pressure and (b) pure helium atmosphere at the ambient pressure.

The initial samples were phase pure YBCO with oxygen content, $x \sim 6{\cdot}9$ and showed a T_c of 90 K. Sample pellets of 10 mm diameter and 1 mm thickness were subjected to the following temperature profile: (a) heating the sample at 50°C/h to reach a desired annealing temperature (T_A), (b) soaking at T_A for 24 h and (c) slow cooling it at the rate of 13°C/h.

2. *In situ* high temperature resistivity studies

Voltage drop across a portion of the sample at a constant current of 60 mA, as well as the temperature of the sample were continuously recorded at every 5 min interval using a PC controlled set up described in Narasimha Rao *et al* (1996).

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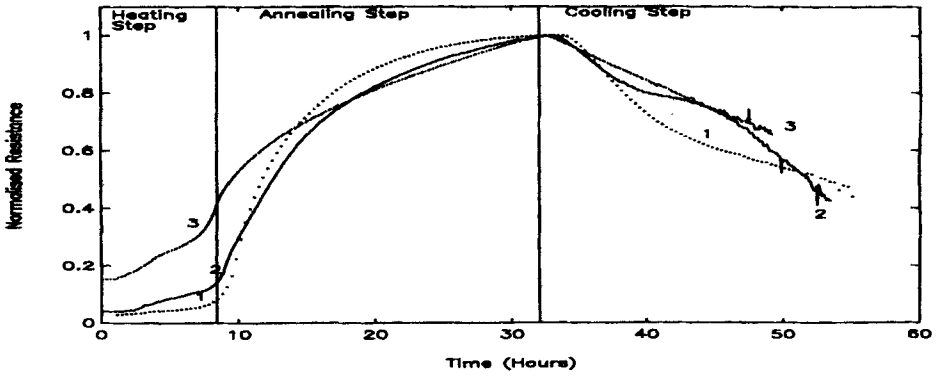

Figure 1. Normalized resistance vs time plot of YBCO in helium atmosphere. Curves 1, 2 and 3 correspond to $T_A = 453°$, 433° and 383°C, respectively.

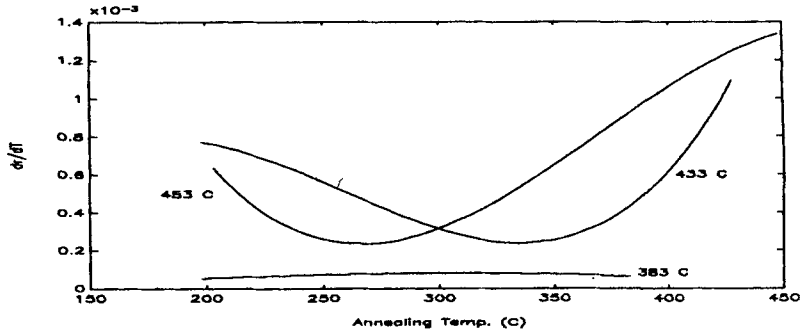

Figure 2. Derivative plot, dR/dT vs annealing temperature in the cooling region.

We present the results of resistivity measurements carried out at the annealing temperatures of $T_A = 383°$, 433° and 453°C in a helium atmosphere. In each case the resistance is normalized with respect to the maximum resistance of the sample and plotted R vs T plot (cf. figure 1), which show several interesting features: (i) increase of resistance in the heating step which may be predominantly due to loss of oxygen, (ii) increase in resistance during soaking at T_A which may be mainly due to the transition from order to disorder in the oxygen configuration and (iii) fall of resistance in the cooling step which may be partially attributed to a fall in resistance due to metallic nature. During cooling, while the 383°C sample has a linear fall of R with T, those for 433° and 453°C show non-linear structure in the R vs T behaviour.

XRD measurements showed that at the end of temperature profile the samples were orthorhombic with oxygen contents 6·55, 6·34, 6·25 respectively as estimated from the known variation of (Blinovskov *et al* 1988) lattice parameter with x. A plot of dR/dT vs temperature in the cooling region is shown in figure 2. We identify the minima in dR/dT curve to be the temperature at which the sample should be annealed for long enough time to promote optimal ordering in YBCO samples.

3. *In situ* high temperature XRD studies

Pellets (5 mm dia and 0·5 mm thick) of phase pure YBCO with oxygen content, $x \sim 6{\cdot}9$ were placed in the cavity provided in the tantalum heater element of the HDK 2·3 sample heater chamber compatible with Siemens D-500 powder diffractometer. Small quantity of silver paste was used to stick the sample pellet to the tantalum sheet to prevent sliding of the sample at high angles during data collection. The chamber was evacuated to 10^{-4} Pa pressure. Samples were subjected to the typical temperature profile described earlier with different annealing temperatures (T_A). The XRD data was

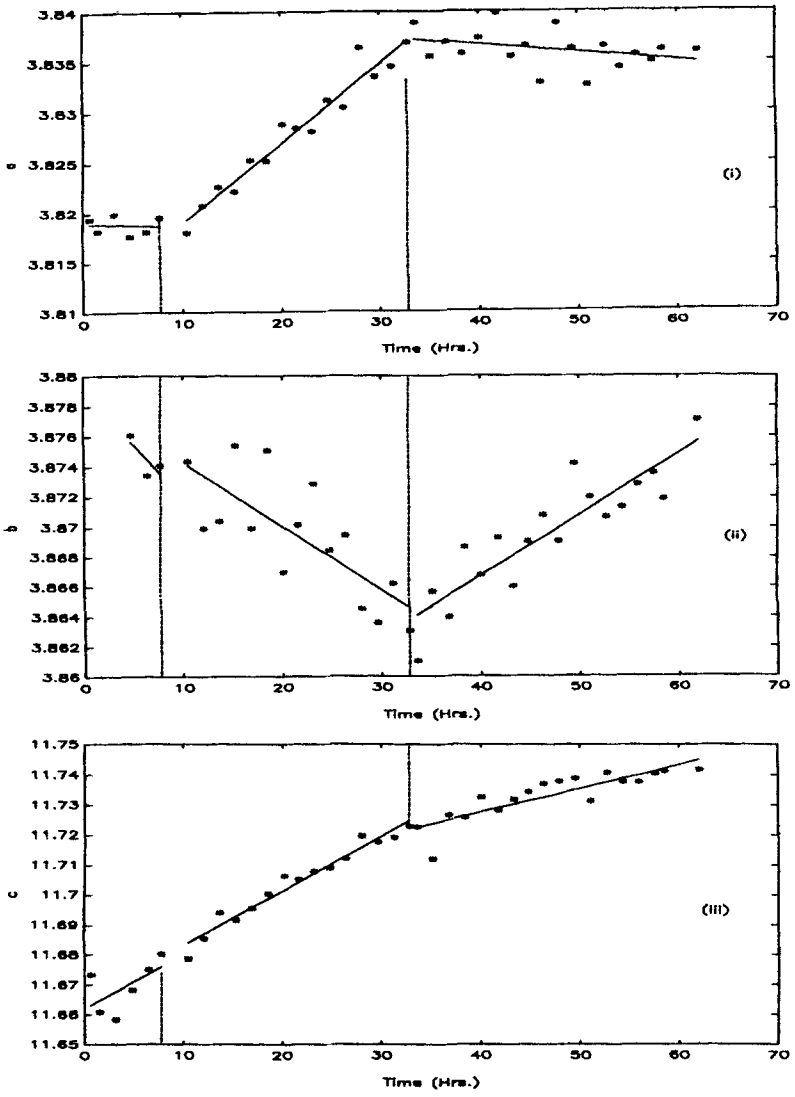

Figure 3. Lattice parameter vs time plot for YBCO sample annealed at 410° C in vacuum, obtained from (i) 200, (ii) 020 and (iii) 006 *hkl* reflections. Vertical dotted lines are drawn to mark the end of heating and annealing steps.

collected by step scan method in the selected 2θ regions of interest (ROI), namely, 22–23·4°, 31·8–33·2°, 37·5–39·0°, 39·6–40·7°, 45·5–48·2°, 55–56° and 57·2–59·2°, at a step size of 0·05°, with dwell time of 22 sec per step. The angle versus counts data was collected in an IBM compatible PC. The data in the 2θ ROI of 46–48° was carefully analyzed to extract the a, b, c lattice parameters using the (200), (020), (006) *hkl* reflections. These results for the sample annealed at 410°C in vacuum are shown in figure 3. These data have been corrected for thermal expansion (using a value of $\alpha = 1{\cdot}8 \times 10^{-6}/°C$) so as to visualize the lattice parameter variation due to oxygen stoichiometry and ordering alone without the complication of thermal expansion.

In the case of sample which is annealed at 410°C, there exists two distinct phases at the end of the cooling step, namely a tetragonal and an orthorhombic phase. The thermal expansion corrected (006) *hkl* reflection of the ortho phase shows an increase in '*c*' lattice parameter from 11·72 to 11·745 Å, whereas the '*b*' lattice parameter increases from 3·862 to 3·878 Å and the '*a*' lattice parameter decreases from 3·840 to 3·835 Å. In the absence of any intake of oxygen from outside, this could be possible only under two situations; (a) if there were a redistribution of the oxygen atoms in the basal plane within the grains and (b) better ordering of the sample during cooling. Low temperature ac susceptibility measurements on the 410°C annealed sample showed a T_c of 60 K which corresponds to the OII phase. Further investigations such as processing of the XRD data in other ROI's to extract thermal expansion parameters along different directions of the YBCO unit cell in vacuum/helium atmospheres as well as TGA/DTA are presently under way to throw more light on the subject.

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