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CORE AND VALENCE LEVEL PHOTOEMISSION STUDIES OF OXYGEN ANNEALED $\text{Y}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n}$ ($n=0,1,2$) SURFACES.

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Atomically clean surfaces of the 123, 247 and 124 Y-Ba-Cu oxide superconductors have been prepared for photoemission studies by *in situ* oxygen annealing. They are characterised by simple lineshapes for the O1s core level in XPS and the absence of satellite structure at 9.5eV in valence level UPS. Atomic ratios inferred from the intensities of XPS core lines demonstrate barium segregation at the surfaces of all three materials.

1. INTRODUCTION.

There has been growing interest in the past two years in the physical properties of the so-called 247 and 124 phases $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$. A feature of particular note is that the 124 phase achieves its full oxygen stoichiometry at the temperature of phase formation¹, unlike the 123 phase $\text{YBa}_2\text{Cu}_3\text{O}_7$ which must be post-annealed in flowing oxygen at low temperatures. The 123 phase is moreover susceptible to oxygen loss under UHV conditions required for electron spectroscopy and many of the ambiguities surrounding early photoemission work on this material appear to be related to its instability in UHV². In the present communication we present a comparative study of the three Y-Ba-Cu phases using the same technique to prepare clean surfaces of each material.

2. EXPERIMENTAL.

Ceramic samples of $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$ were prepared by established procedures, using a NaNO_3 accelerant to facilitate formation of the 247 and 124 phases³. Phase purity was established by X-ray powder diffraction. Four probe conductivity measurements showed onsets of the superconducting transitions for the 123, 247 and 124 phases at 92K, 92K and 79K respectively, with zero resistance at 91K, 84K and 75K.

Photoemission measurements were carried out in an ESCALAB Mk II electron spectrometer.

In situ cleaning to remove sodium, hydrocarbon, carbonate and hydroxide contamination was achieved by annealing samples for c.a. 1 hour at 600°C in 1 atmosphere of pure oxygen in a preparation chamber forming an integral part of the spectrometer UHV system. Careful regulation of surface temperature was achieved using an emissivity calibrated infrared pyrometer viewing the front face of the sample. After cleaning the samples were allowed to cool to around 400°C and the preparation chamber was then evacuated rapidly down to UHV pressures with the sequential aid of a rotary backed turbomolecular pump and a liquid nitrogen trapped oil diffusion pump. In view of the high diffusion coefficient for oxygen even at 400°C the surfaces are not necessarily fully oxygenated, but the surface cation distribution established during *in situ* annealing should be preserved.

3. RESULTS AND DISCUSSION.

The results of *in situ* annealing on the O:1s core level structure is illustrated in fig. 1 for $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$. Similar data were obtained for $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$. The high binding energy component of the original O:1s core line is strongly attenuated, supporting the now widely accepted view that high binding energy structure is not intrinsic to Y-Ba-Cu oxide phases². Likewise on incompletely cleaned surfaces, a strong peak was found in He(II) ($h\nu=40.8\text{eV}$)

FIGURE 1

Al K α XPS of $Y_2Ba_4Cu_7O_{15}$ in O1s core region (a) before and (b) after in situ oxygen annealing.

spectra at 9.5eV binding energy, but this is strongly reduced upon in situ cleaning (figure 2). The peak reappeared upon exposure of sample surfaces to water, even for exposures as low as 10L. Thus we believe the satellite intensity to be associated with adsorbed OH $^-$ groups, as suggested previously⁴.

Effective atomic compositions of the 123, 124 and 247 surfaces as probed by XPS were derived by

FIGURE 2

He(II) ($h\nu=40.8\text{eV}$) excited valence band photoemission of $YBa_2Cu_4O_8$ showing residual hydroxide contamination (a) and after prolonged in situ cleaning by oxygen annealing. Note diminution of 9.5eV satellite in (b).

correcting XPS intensities for atomic sensitivity factors, as shown in figure 3. All of the surfaces show some enrichment in Ba relative to Y and Cu, the effect being particularly strong for the 247 and 124 phases. Deviation from ideal stoichiometry can arise in photoemission measurements from layered materials due to preferential surface termination in one particular ionic plane. The Ba enrichment is too pronounced in these cases to be accounted for simply by termination of the ceramic in BaO planes of the bulk crystal structure. Thus despite atomic cleanliness, the surfaces of oxygen annealed 124 and 247 phases are not representative of the bulk stoichiometry.

FIGURE 3

Block diagram showing atomic ratios of Y Ba and Cu in 123, 247 and 124 superconducting phases derived from core level XPS. For the 124 phase data were taken at both normal and grazing (15°) emission angle.

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