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Observation of carboxylic groups in the lattice of sintered $Ba_2YCu_3O_{7-y}$ high-T_c superconductors

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This study reports for the first time the experimental evidence that stable carboxylic groups are present in the lattice of sintered $Ba_2YCu_3O_{7-y}$ superconducting oxides. The carboxylic groups likely originated in the incomplete calcination of the $BaCO_3$ precursor powder and they could be responsible for the oxygen over-stoichiometry observed in these materials. Further experimental investigations are required concerning in particular the sites of carboxylic groups in the Ba-Y-Cu-O lattice and their effects on the tetragonal-orthorhombic instability.

A key question in understanding the mechanisms responsible for the high critical temperature, T_c, in cuprate superconductors[1-5] is the knowledge of the crystallographic and electronic structure of the superconducting phase.[6,7]

Several theoretical and experimental papers have been already published on this subject;[8-11] however, some fundamental problems such as the mechanisms of the tetragonal-orthorhombic instabilities[7-12] and the origin of the O over-stoichiometry, are still unresolved.[13,14]

The purpose of this paper is to present Auger and x-ray photoelectron spectroscopy (XPS) studies on $Ba_2YCu_3O_{7-y}$ sintered compounds with a view to search for possible segregated phases or impurities that might influence the structural stability. For the first time unambiguous data on the presence of carboxylic groups in the Ba-Y-Cu-O lattice are provided.

Samples with nominal composition $Ba_2YCu_3O_{7-y}$ were prepared by mixing the reagent powders and grinding and firing them using a quartz crucible in O_2 flow at 980 °C for 8 h. After the first firing the compound was reground and the calcination process repeated several times. The master powder was then pressed in pellets of 20 mm in diameter and 3 mm thick and sintered at 980–1000 °C in O_2 flow for 8 h, then cooled at room temperature over a period of 12 h.

The sample structure was tested by x-ray diffraction (XRD) and x-ray fluorescence to determine the crystallographic phase and the chemical composition. All the samples corresponded to the $Ba_2YCu_3O_{7-y}$ stoichiometry with y ranging between 0.2 and 0.1 and showed a perovskitelike single phase structure with a tripled c axis ($c = 11.685$ Å) and a small orthorhombic distortion ($a = 3.820$ Å and $b = 3.887$ Å). No extra reflections were found in the XRD pattern.

Electrical resistance measurements, made in a conventional four-probe configuration using silver paint contacts, gave a T_c at 91 K with a (10%–90%) transition width of 2 K.[15]

Two rectangular bars of $18 \times 3 \times 3$ mm^3 were cut from the pellets; one was introduced into the ultrahigh-vacuum (UHV) preparation chambers of a scanning Auger microscopy (SAM) apparatus and the other into a high-resolution XPS system.

The SAM apparatus was a Perkin-Elmer Model 660 with a spatial resolution of 300 Å, while the XPS apparatus was a 5400 Perkin-Elmer standard photoelectron spectrometer equipped with a x-ray monochromator and a multichannel electron detector. The ultimate resolution of this system, at a pass energy of 4.5 eV on the Si $2p_{1/2}$ and Si $2p_{/2}$ was 360 meV using the Al $K\alpha$ radiation. The spectrometer was calibrated with the Ag $3d_{5/2}$, Cu $2p_{3/2}$, and Au $4f_{7/2}$ core-level lines, at which the following binding energies, E_B, 367.9 eV, 932.4 eV, and 83.8 eV were assigned, respectively.

The superconductor bars were then cleaved in UHV at 10^{-8} Pa and the central part of the fractured surfaces was analyzed on an area of 1 mm^2, by SAM and XPS.

In spite of the deep calcination process, repeated several times in order to minimize the C in the system, all samples exhibited a significant amount of this element.

To control possible segregated phases and inhomogeneities, particularly metal-CO_3 or M-CO_x compounds, a higher spatial resolution (≈ 300 Å) Auger map of the C was performed. The SEM micrographs of the fractured area showed about 40% of grain boundary surface and 60% of intragranular surface. Within the resolution of the apparatus, repeated measurements indicated a uniform distribution of the C. Figure 1 shows the first derivative, dN/dE, of the KVV Auger spectrum of the C detected on an area containing mainly cleaved grains. The shape and the kinetic energies of the main spectral lines, KL_1L_1 (^1S), KL_1L_{23} (^1P), and $KL_{23}L_{23}$ (^1D) are significantly different from those of the Auger spectrum of the graphitic C.[16] Particularly, the fine structures labeled X_1 and X_2, whose shape and energy reflect the local density of atomic states near the C atoms, are due to interatomic transitions typical of Auger processes in C compounds chemisorbed on metal surfaces.[17,18] In Ba-Y-Cu-O sintered superconductors, such an effect can be originated by carbidic (M-C) or carboxylic groups (M-CO_x) arising from an incomplete calcination process of the precursor

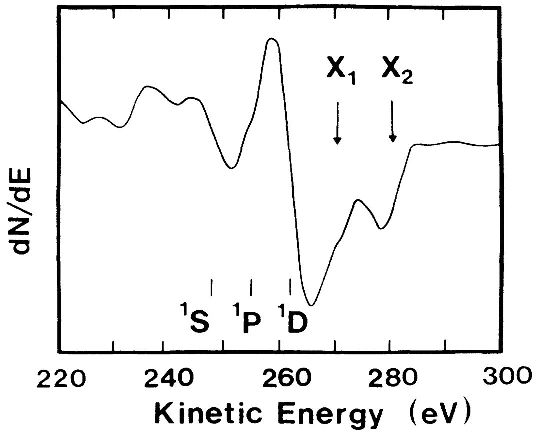

FIG. 1. The *KVV* Auger spectrum of the C detected on UHV cleaved surfaces of sintered $Ba_2YCu_3O_{7-y}$ superconductor is shown in the *dN/dE* derivative mode. Identified spectral terms are reported in order of increasing kinetic energy $KL_1L_1(^1S)$, $KL_1L_{23}(^1P)$, and $KL_{23}L_{23}(^1D)$. The two fine-structure lines are due to interatomic transitions.

$BaCO_3$ powder. This result agrees with recent thermogravimetric studies and evolved gas analysis performed on $Ba_2YCu_3O_{7-y}$ sintered superconductors.[19]

More detailed information on the chemical state of the C were obtained by XPS. Figure 2(a) shows the XPS spectrum of the C 1*s* core level. A multiple peak structure with two main bands centered at 289.0 and 284.5 eV, are observed. XPS band-structure deconvolution[20] allowed identification of at least another band at 285.6 eV, in the energy range between 291.0 eV and 285.0 eV.

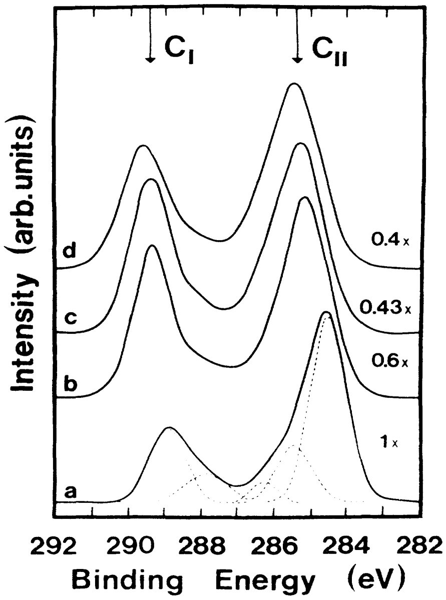

FIG. 2. High resolution XPS spectra of the C 1*s* detected on UHV fractured surfaces of sintered $Ba_2YCu_3O_{7-y}$ superconductors: (a) as detected on the surface fractured in UHV; (b) after Ar^+ sputtering equivalent to about 5 Å of depth profile; (c) after 50 Å of depth profile; (d) after 150 Å of depth profile.

SEM observations of the fractured area suggest that the peak at lower E_B, i.e., 284.5 eV, could be attributed to hydrocarbon contaminations present even on UHV fractured surfaces because of the high porosity of this material. On the other hand, the multiple peak structure between 285.0 and 291.0 eV, indicated with C_I and C_{II}, is consistent with theoretical and experimental XPS data of CO molecules chemisorbed on metal surfaces[21-24] and it confirms the interpretation of the *KVV* Auger spectrum achieved on Ba-Y-Cu-O cleaved grains. Particularly, the peak at 285.6 eV could arise from a transition in which the final state is given by an unoccupied $2\pi^*$ derived level of CO pulled, by the core hole, below the Fermi level of the metal and filled by an electron from the metal valence band.[24] Following this interpretation, the peak at 289.0 eV originates from transitions to a final state in which the screening orbital is not filled. The presence of more than two peaks can be explained with the presence of more than one screening orbital.

Since no significant structures were detected in the C 1*s* E_B region below 284.0 eV *M*-C (carbidic) bonds should be excluded[25,26] and, unambiguously, the chemical status of the bound carbon have to be identified with carboxylic groups (M-CO_x).

Further indications were obtained by sputtering the fractured surface. Ion bombardment of the sample by Ar^+ at 1 KeV with a current of 1 mA allowed a sputtering rate of about 0.5 Å/sec. With these parameters the preferential sputtering was significant for the C, very low for the O and almost irrelevant for Y, Ba, and Cu. After 10 sec of ion bombardment, equivalent to ≈ 5 Å of depth profile, the total C atoms percentage was reduced by about 30%, while the C 1*s* XPS spectrum, as shown in Fig. 2(b), was changed. The disappearance of the peak at 284.5 eV, due to the sputtering of hydrocarbon surface contaminants, allowed the rise up of the multiple peak structure. This structure is very similar to that detected on the unsputtered surface [Fig. 1(a)]. Deeper sputtering, at 50 and 150 Å as reported in Figs. 2(c) and 2(d), does not produce further qualitative evolutions of C 1*s* XPS spectra, while it confirms the trend previously observed.

Finally, the persistency, after a deep sputtering, of the multiple peak structure in the C 1*s* spectra firmly establishes the existence of carboxylic groups in the Ba-Y-Cu-O lattice.

It is of interest now to speculate on the influence of carboxylics groups on the structural instabilities observed in these compounds in view of possible correlations between the crystallographic structure and electronic phase transitions. Furthermore, the origin of anomalous position parameters of the O (Ref. 12) together with the O overstoichiometry should be examined in light of these results.

In conclusion, this experiment gives special attention to the chemical status of the C present in sintered Ba-Y-Cu-O superconducting systems and the main result obtained is the presence of M-CO_x groups in the lattice of such compounds.

A crucial unanswered question is that which concerns the influence of these groups on superconductivity mechanisms.

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