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  13. The sign of the hyperfine coupling constants for the oxovanadium complexes are known to be minus (ref. 8), but it has been neglected in this paper.

## An XPS Study of YBaCuO Compounds

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*Received October 23, 1989*

X-ray photoelectron spectra have been obtained and comparisons have been made for 1-2-3 and 2-1-1 phases of YBaCuO compounds. The photoelectron binding energies of all the constituent elements are consistently larger for the 2-1-1 phase than for the 1-2-3 phase. The peak intensities reflect different stoichiometries of the two phases. For the superconducting 1-2-3 phase, its degradation in air and interaction with water and carbon dioxide were examined by taking core level spectra of all the elements. It appears that yttrium is the most affected by exposure to air, since it undergoes a rapid change to carbonate when water and subsequently carbon dioxide are introduced.

### Introduction

Since the discovery of YBaCuO superconductor with  $T_c$  higher than 90K, efforts have been made to elucidate the crystal and the electronic structures of the superconducting material. The study of the electronic structures of this high temperature superconductor by use of X-ray photoelectron spectroscopy has contributed much to the explanations of various phenomena such as the superconducting mechanism, effect of temperature,<sup>1,2</sup> and degradation in air.<sup>3</sup> As is well known, the YBaCuO superconductor is quite unstable in air, which will cause difficulties in its utilization. For the application of YBaCuO superconductor to be successful, it is necessary to understand its degradation mechanism. To this end, a careful examination of the changes of the superconductor surfaces is required.

The nonsuperconducting 2-1-1 phase has rarely been studied by XPS, but since it is often formed during the preparation of the 1-2-3 phase and is also considered to be a good candidate substrate for the 1-2-3 phase film, it will be quite informative to investigate the spectral differences between this phase and the superconducting 1-2-3 phase. In this study, the core orbital binding energies of the elements in 1-2-3 and 2-1-1 phases of YBaCuO compounds were determined and compared. To investigate the degradation mechanism of the 1-2-3 phase in air, spectral changes of the material were examined with time it was kept in air. The interaction of the material with water and carbon dioxide was also studied.

### Experimental

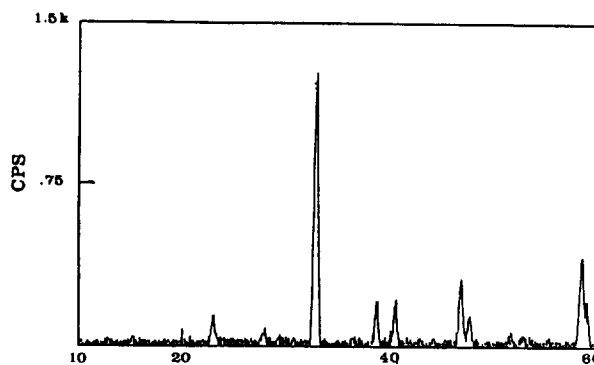


Figure 1. XRD pattern of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

To prepare the 1-2-3 phase,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , we used  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  powders purchased from Aldrich Chemical Company, Inc. without purification. The powders were pressed into pellets at 13600 psi. The pellets were then sintered at 950 °C in flowing oxygen for 2 hours. From X-ray diffraction pattern of the sintered body, it was found to consist of the 1-2-3 single phase only (Figure 1). The 2-1-1 phase was made by pressing the equimolar mixture of  $\text{Y}_2\text{O}_3$ ,  $\text{Ba}(\text{OH})_2$ , and  $\text{CuO}$  powders into pellets at 13500 psi followed by calcination at 900 °C for 18 hours and sintering at 940 °C for 24 hours.<sup>4</sup> The phase of the final product was confirmed to be 2-1-1, also by XRD as shown in Figure 2.

The samples thus prepared were transferred into the fast entry airlock of the ESCALAB MK II (VG Scientific Ltd.) and scraped by a diamond file to expose clean surfaces. The pressure of the airlock was maintained at  $10^{-8}$  torr during

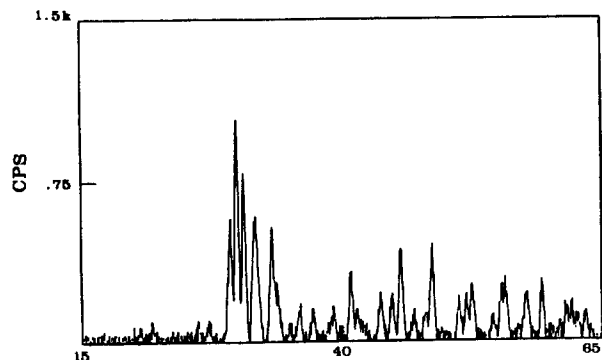


Figure 2. XRD pattern of  $Y_2BaCuO_5$ .

scraping. Immediately after scraping the samples were moved into the analysis chamber for XPS analysis at pressures below  $10^{-9}$  torr.

Degradation of the 1-2-3 phase was examined with samples exposed to air for 5 minutes up to 3 weeks. Interaction of this phase with water was studied for a sample exposed to water vapor at  $10^{-5}$  torr for 5 minutes and subsequently at 25 torr for 5 minutes. The water vapor was generated from distilled water out-gassed by repeated freezing and thawing with pumping in between.

Table 1 is a summary of the analysis conditions and photoelectron peaks examined. Binding energies were calibrated with reference to Au  $4f_{7/2}$  peak (83.8 eV) taken from gold deposited on the sample surfaces to 20 nm thickness using a *dc* magnetron sputtering machine (Polaron Equipment

Table 1. Analysis Conditions and Peaks Analyzed for YBaCuO Compounds

Items	Analysis conditions	Elements	Peaks
Pressure	$< 10^{-9}$ torr		
Analyzer type	Spherical sector	Yttrium	$3d$
X-ray source	Mg $K\alpha$ (1253.6 eV)	Barium	$3d_{5/2}$
X-ray power	300 W (15 kV, 20 mA)	Copper	$2p_{3/2}$
Analysis area	1 cm $\times$ 1 cm	Oxygen	$1s$
Step size	0.05 eV	Carbon	$1s$
Dwell time	50 ms	Gold	$4f_{7/2}$
Pass energy	50 eV		

Limited). Data acquisition and analysis were carried out by a PDP-11 Micro/rsx computer from Digital Equipment Corporation. The spectra were smoothed using the method of least squares except for C  $1s$  due to low intensity and excessive noise.

## Results and Discussion

### The electronic structure of the 1-2-3 phase YBaCuO.

After scraping the sample with a diamond file, the C  $1s$  region was examined to ascertain the cleanliness of the surface. The C  $1s$  peak could be seen but with low intensity, so the sample was considered clean enough for XPS experiments. Photoelectron spectra of Y, Ba, Cu, and O for this surface are shown in Figure 3.

In the Cu  $2p$  region of the 1-2-2 phase, the main peak

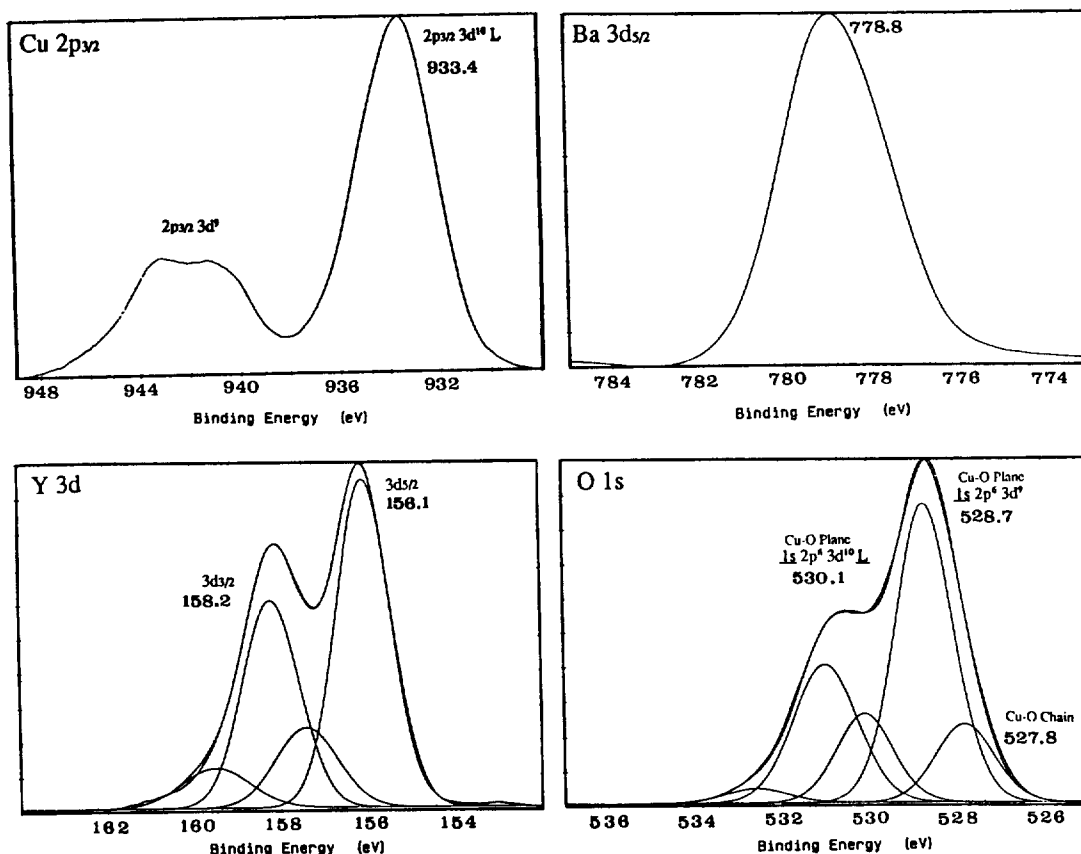
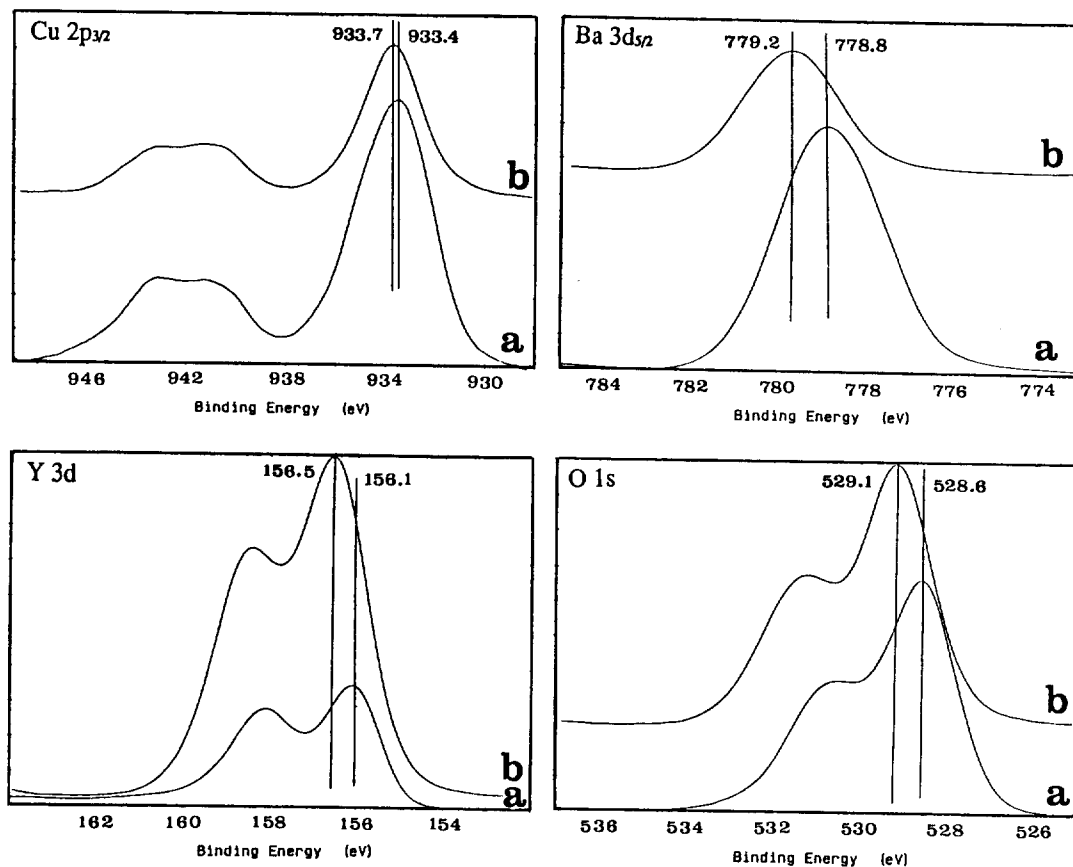


Figure 3. Photoelectron spectra of  $YBa_2Cu_3O_{7-x}$  surface cleaned by scraping with a diamond file.



**Figure 4.** Comparison of 1-2-3 phase and 2-1-1 phase. (a) 1-2-3 phase, (b) 2-1-1 phase.

( $2p_{3/2}3d^{10}L$ ) appears at 933.4 eV with a broad satellite structure ( $2p_{3/2}3d^9$ ).<sup>5-7</sup> The binding energy (BE) of the main peak is about 0.2 eV smaller than that for CuO (933.6 eV). As discussed by Steiner *et al.*<sup>8,9</sup> no structures indicating the presence of  $\text{Cu}^{3+}$  seem to exist except that the main peak is rather broad. According to many studies reported so far, in the case of XPS experiments, it is not possible to identify  $\text{Cu}^{3+}$  or inequivalent Cu sites (Cu in Cu-O plane and Cu-O chain) because of inherent final-state effects,<sup>10</sup> or because the charge within the Cu site is very nearly the same for all Cu atoms.<sup>11</sup>

Ba  $3d_{5/2}$  level (BE = 778.8 eV) is 0.8 eV smaller than BaO (BE = 779.6 eV) and its half-width is somewhat wider. Y  $3d$  level (BE = 156.1 eV) is 0.3 eV smaller than  $\text{Y}_2\text{O}_3$  (BE = 156.4 eV) and shows a wide doublet. The Y  $3d$  region is separated into two doublets by curve synthesis. The one with the larger binding energy is thought to be due to carbonates.

The interpretation of the O 1s spectrum has been controversial. Sarma *et al.* reported presence of peroxide,<sup>12</sup> but, in our experiments, there appear three peaks corresponding to Cu-O plane state (528.7 eV), Cu-O chain state (527.8 eV), and shake-up structure (530.1 eV) of Cu-O plane as found by Weaver *et al.*<sup>3</sup> In addition there are two more peaks to the left of 530.1 eV. They are probably due to carbonates and oxides on contaminated grain boundaries,<sup>3,13</sup> which is in accordance with the fact that half-widths of various peaks are relatively wide and the surface is contaminated with carbon to some extent.

**Comparison of the 1-2-3 and 2-1-1 phases.** The surface electronic structures of the impurity phase  $\text{Y}_2$

$\text{BaCuO}_5$ , which is often found in the process of preparing the 1-2-3 phase  $\text{YBaCuO}$  were studied and compared with those of the 1-2-3 phase. As shown in Figure 4, the peaks for Cu, Ba, and Y appear at places where typical oxides (CuO, BaO,  $\text{Y}_2\text{O}_3$ ) show their peaks. The O 1s peak is seen near CuO peak position (BE = 529.2 eV). The distinguishing feature of the 2-1-1 phase compared to the 1-2-3 phase is the relative intensities of various peaks. In the 2-1-1 phase spectra, Y  $3d$  peak is larger, and Ba  $3d$ , Cu  $2p$ , and O 1s peaks are smaller than the corresponding peaks of the 1-2-3 phase. This results from different stoichiometries of the two phases. The binding energies of all the elements of the 2-1-1 phase are 0.3-0.5 eV larger than those of the 1-2-3 phase. The grain boundaries of the 2-1-1 phase also appear contaminated by carbonates judging from the O 1s and C 1s peaks.

**Degradation of the 1-2-3 phase  $\text{YBaCuO}$  in air.** The 1-2-3 phase  $\text{YBaCuO}$  is very unstable in air and its surface easily undergoes degradation,<sup>10</sup> which will cause difficulties in the applications of the  $\text{YBaCuO}$  films. Figure 5 shows changes in the core level spectra of a clean 1-2-3  $\text{YBaCuO}$  sample with time. The Cu  $2p_{3/2}$  peak shifts towards higher binding energy, its half-width widening with time. Its intensity decreases with time. In the Ba  $3d_{5/2}$  region, peaks corresponding to BaO (BE = 779.6 eV) and  $\text{BaCO}_3$  (BE = 781.3 eV) grow and the peak due to the Ba of the 1-2-3 phase (BE = 778.8 eV) decreases. In the case of Y  $3d$  level, spectral changes also indicate peak shift towards higher binding energy, decrease in peak intensity of the 1-2-3 phase (BE = 156.1 eV), and increase in half-width.

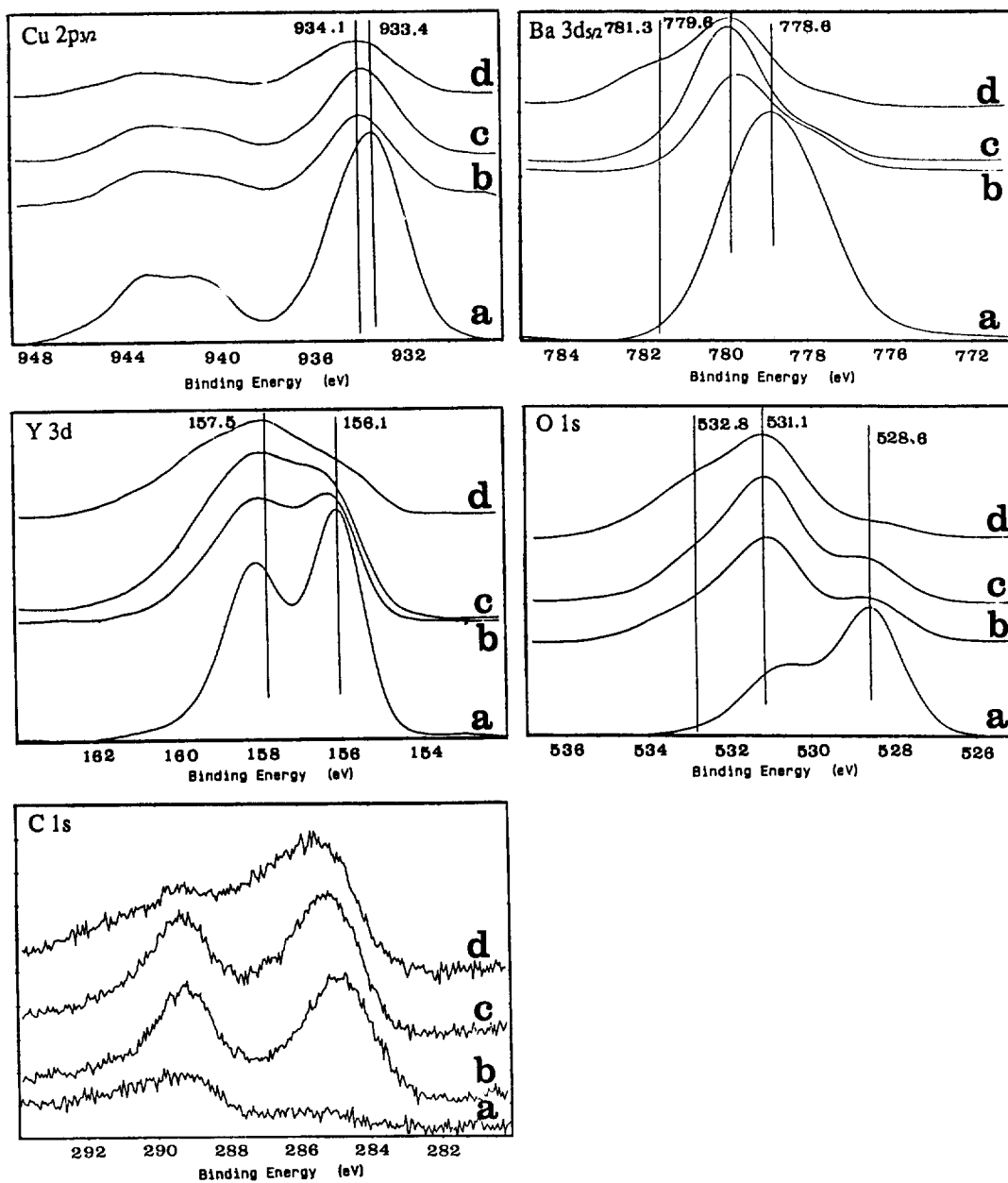


Figure 5. Degradation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in air. (a) clean, (b) 5 min, (c) 1 day, (d) 1 month.

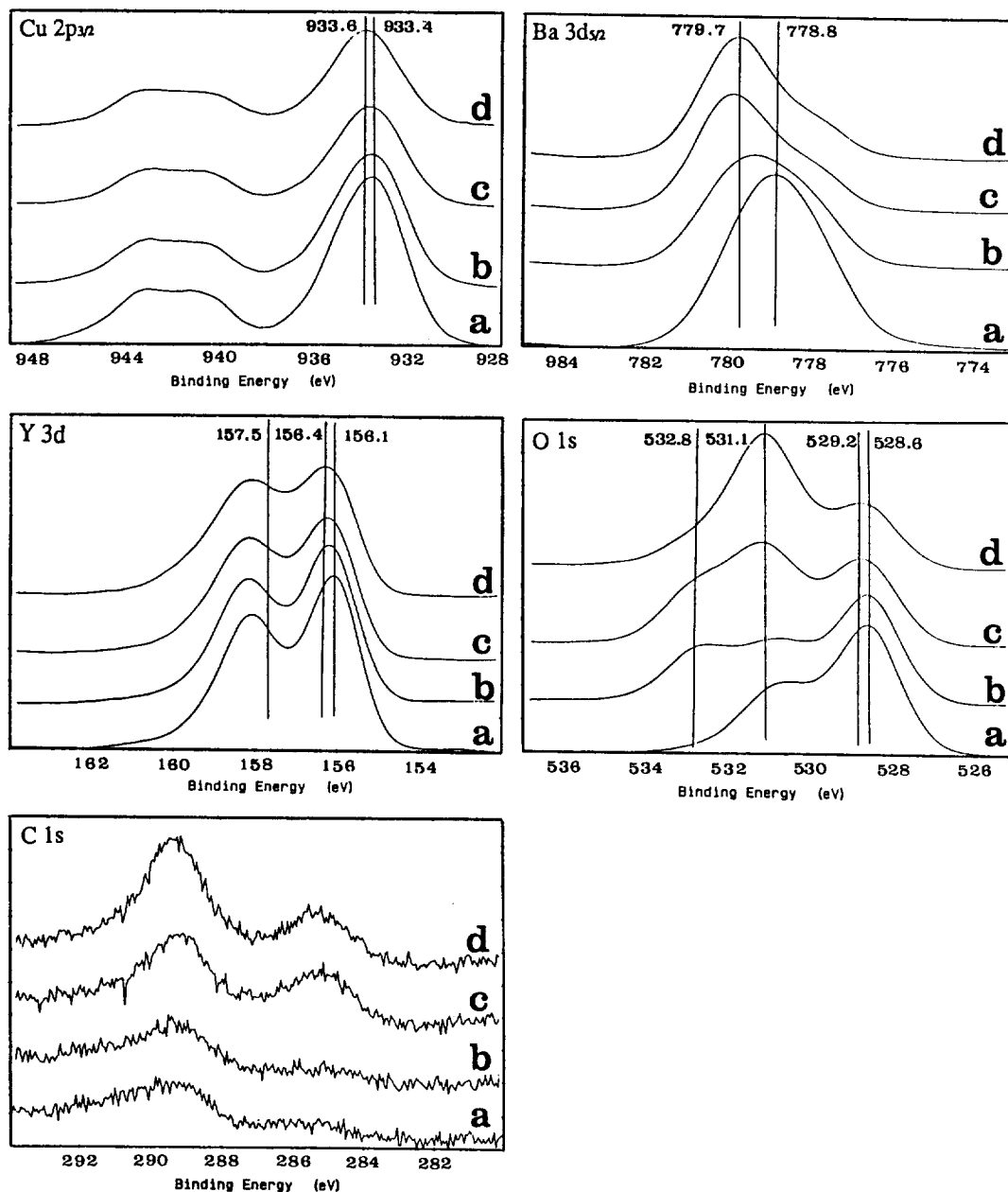
Table 2. Atomic Ratios of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  from Angle Resolved XPS

Elements	Y	Ba	Cu	O	C	
Take-off angle	90°	0.9	2.0	2.1	10.9	3.9
	20°	0.9	2.0	2.1	18.5	20.1

These changes are thought to be due to the formation of oxides and carbonates on the 1-2-3 phase in air, which is manifested by the changes in O 1s and C 1s structures. The O 1s region shows increases in peak intensities corresponding to  $\text{Y}_2(\text{CO}_3)_3$  (BE = 531.1 eV) and  $\text{BaCO}_3$  (BE = 532.8 eV) and decrease of the 1-2-3 phase peak (BE = 528.6 eV). C 1s level shows abrupt increase in peak intensity. To see if the concentrations of Cu, Ba, and Y change in the vertical direction during degradation of the 1-2-3 phase, photoelectron spectra were taken with two different take-off angles for a sample

exposed to air for 24 hours. Table 2 shows that the stoichiometry for the metals remains the same, but O 1s and C 1s peaks are much larger for 20° than for 90°. This indicates that there is no relative concentration change of the metals but carbonates are continuously formed in the surface region. It is interesting to note that once the surface is exposed to air the stoichiometric ratio of copper is no longer 3. The ratio becomes 2.1 as shown in Table 2.

**Interaction of the 1-2-3 phase with water and carbon dioxide.** To understand the degradation mechanism of the 1-2-3 phase YBaCuO in air we examined its interaction with water, since water is reportedly the main cause of the degradation. A cleaned surface was first exposed to water vapor at  $10^{-5}$  torr for 5 minutes, and then at 25 torr for 5 minutes. This was followed by exposure to  $\text{CO}_2$  at 25 torr for 5 minutes. Photoelectron spectra were taken for each step (Figure 6).



**Figure 6.** Interaction of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with water and  $\text{CO}_2$ . (a) clean, (b)  $\text{H}_2\text{O}$ ,  $10^{-5}$  torr, 5 min, (c)  $\text{H}_2\text{O}$ , 25 torr, 5 min, (d)  $\text{CO}_2$ , 25 torr, 5 min.

The  $\text{Cu } 2p_{3/2}$  region shows a peak shift towards  $\text{CuO}$  position ( $\text{BE} = 933.6 \text{ eV}$ ) as the partial pressure of water is increased, but there is no detectable change on contact with  $\text{CO}_2$ . In  $\text{Ba } 3d_{5/2}$  region, there is also a peak shift to the  $\text{BaO}$  position ( $\text{BE} = 779.6 \text{ eV}$ ). After exposure to  $\text{CO}_2$ , the peak shift is about  $-0.2 \text{ eV}$ . In  $\text{Y } 3d$  region, the peaks move to  $\text{Y}_2\text{O}_3$  position ( $\text{BE} = 156.4 \text{ eV}$ ), however, there appears a structure, probably due to carbonate, between  $3d_{3/2}$  and  $3d_{5/2}$  peaks. Contact with  $\text{CO}_2$  accelerates this process. Formation of the carbonate of Y is strongly suggested by the increase of the peak that corresponds to  $\text{Y}_2(\text{CO}_3)_3$  ( $\text{BE} = 288.9 \text{ eV}$ ) in the C 1s region. The peak at  $285 \text{ eV}$  is probably due to carbon contamination.

In O 1s region, it is clear that the peaks suggesting the presence of  $\text{CuO}$  ( $\text{BE} = 529.2 \text{ eV}$ ) and  $\text{BaO}$  ( $\text{BE} = 531.1 \text{ eV}$ ) grow with the partial pressure of water. Among the O 1s peaks, the one that appears at  $532.8 \text{ eV}$  after contact with

water disappears on exposure to  $\text{CO}_2$ . The peak at  $531.1 \text{ eV}$  grows instead. This change and the change in peak position of  $\text{Ba } 3d_{5/2}$  ( $-0.2 \text{ eV}$ ) are both caused by  $\text{CO}_2$  exposure, and are believed to be closely related to the carbonate formation. At this stage, we cannot quite understand the mechanism. Further experiments are necessary for the explanation of these changes.

According to the papers published so far the 1-2-3 phase interacts with water to decompose into  $\text{CuO}$ ,  $\text{Ba}(\text{OH})_2$ , and  $\text{Y}(\text{OH})_3$  and, after absorbing  $\text{CO}_2$ , forms  $\text{BaCO}_3$  and  $\text{Y}_2(\text{CO}_3)_3$ . It is also believed that the 2-1-1 phase is formed in this process.<sup>13,14</sup> On the other hand, the compound  $\text{CuO}$  transforms into  $\text{CuCO}_3$  after prolonged exposure to air. A peak with binding energy higher than that of the main  $\text{Cu } 2p_{3/2}$  peak appears in this case. For  $\text{CuCO}_3$  to be formed, the formation of  $\text{Cu}(\text{OH})_2$  seems necessary. Our result, however, does not show a peak at  $935.1 \text{ eV}$  for hydroxide and the satellite peak

**Table 3.** Binding Energies (eV) for Elements in Various Compounds

Compounds	Cu 2p <sub>3/2</sub>	Ba 3d <sub>5/2</sub>	Y 3d <sub>5/2</sub>	O 1s	C 1s
1-2-3 phase <sup>a</sup>	933.4	778.8	156.0	528.6	—
2-1-1 phase <sup>a</sup>	933.7	779.7	156.5	529.1	—
CuO <sup>c</sup>	933.6	—	—	529.2	—
Cu(OH) <sub>2</sub> <sup>c</sup>	935.1	—	—	—	—
CuCO <sub>3</sub> <sup>c</sup>	935.0	—	—	—	—
BaO <sup>b</sup>	—	779.6	—	—	—
Ba(OH) <sub>2</sub> <sup>a</sup>	—	781.3	—	534.3	—
BaCO <sub>3</sub> <sup>a</sup>	—	781.1	—	532.8	290.0
Y <sub>2</sub> O <sub>3</sub> <sup>b</sup>	—	—	156.4	528.6	—
Y <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>a</sup>	—	—	157.5	531.1	288.9

a: peak measured relative to Au 4f<sub>7/2</sub>, b: reference 15, c: reference 16

does not change either. In the case of Ba there is no hydroxide peak. The changes in the O 1s region show no indication of hydroxide peaks of Cu and Ba. Therefore at least in the initial stage of the interaction with water, the 1-2-3 phase does not seem to form hydroxides of Cu and Ba. This is corroborated by the fact that the sample that has undergone surface changes by water does not show any detectable change in Cu 2p<sub>3/2</sub> structure and there appears no peak corresponding to BaCO<sub>3</sub> in the Ba 3d<sub>5/2</sub> region. In the case of Y the carbonate peak increases with water partial pressure and the CO<sub>2</sub> exposure accelerates this process. It is therefore thought that, although not detectable, yttrium hydroxide is formed by water and reacts with a small amount of CO<sub>2</sub> or CO to produce carbonates. With our XPS results it is not possible to detect the formation of the 2-1-1 phase. If the surface of the 1-2-3 phase YBaCuO changes to the 2-1-1 phase, the change in the relative peak intensities of Y, Ba, and Cu should be seen. This was not detected.

From the results of our study we can draw the following conclusions. The XPS result does not identify the formation of Cu<sup>3+</sup> or peroxide purported by some early researches. The peaks of Y, Ba, and Cu have relatively wide half-widths due to carbonates on contaminated grain boundaries. The 2-1-1 phase has binding energies greater than those of the 1-2-3 phase for all the elements by 0.3–0.5 eV. The degradation of the 1-2-3 phase by air or water is very complicated indicating formation of mixed oxides of Cu and Ba and hydroxide of Y. Yttrium hydroxide is not detectable but rapid formation of carbonate species strongly suggests its transient formation. It is thought that carbonates of Ba and Cu are not formed in the initial stage of degradation. Among the metals, yttrium appears to be the most unstable in air.

**Acknowledgement.** This study was funded by the Ministry of Science and Technology. The authors wish to express their gratitude for the financial support.

## Appendix

To analyze the XPS data it was necessary to find binding energies for various compounds. They are shown in Table 3.

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